A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. II.

A DICTIONARY

OF

APPLIED CHEMISTRY

BY

Sir EDWARD THORPE, C.B., LL.D., F.R.S.

EMERITUS PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES
OF THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, LONDON;
LATE PRINCIPAL OF THE GOVERNMENT LABORATORY, AND A PAST PRESIDENT OF
THE CHEMICAL SOCIETY AND OF THE SOCIETY OF CHEMICAL INDUSTRY

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annalen der Physik.
Ann. Physique	Annales de Physique.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Weekblad.	Chemisch Weekblad.
Chem. Zeit	Chemiker Zeitung.
Chem Zentr	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Han'.	Fluckiger and Hanbury. Pharmacographia.
Frdl.	Friedlander's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Jahrb. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
J. Amer Chem. Soc.	Journal of the American Chemical Society.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Frankl'in Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Met & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung.

Phil. Mag.	Philosophical Magazine (The ~~London~~)
Phil. Trans. . . .	Philosophical Transactions of the Royal Society
Phot. J.	Photographic Journal.
Proc. Roy. Soc. .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim. . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr.	
Genussm . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl.	
Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal.	
Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandt-
	schaftslehre.
Zeitsch. physiol.	
Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

LIST OF CONTRIBUTORS

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CALAFATITE v. Ai NITE.

CALCULI v. URINE.

CALCUSOL. Trade name for a preparation of acid potassium carbonate and piperidine-p-sulphamine benzoate

CALIATURWOOD. This wood, the botanical origin of which appears to be unknown, is very similar to though somewhat darker in colour than sanderswood. It was imported from the East Indies and is stated to have been chiefly employed in the Continent. According to Franchimont and Sicherer it contains santalin but in larger amount than sanderswood.

CALICHE. The term by which the impure native sodium nitrate or Chile saltpetre is known throughout South America. Also applied to a limestone hardpan found in Arizona and elsewhere (v. SODIUM).

CALLISTEPPIN v. ANTHOCYANINS.

CALLUTANNIC ACID v. TANNINS.

CALMATAMBIN v. GLUCOSIDES.

CALMONAL. Calcium methylbromide.

CALOMEL. Mercurous chloride (v. MERCURY).

CALOMELOL. A colloidal preparation of calomel.

CALOPHYLLUM iNOPHYLLUM (Linn.). A tree (ord. Guttiferæ), Alexandrian laurel, dilo of Fiji, tamanind of E. Polynesia, and sultana champa (Hind.) of India), the seeds of which yield 60 p.c. of a fragrant green oil, fluid at ordinary temperatures, solidifying when cooled below 10°. The tree bears fragrant white flowers. The oil, the woondel or bitter oil of Indian commerce, used in medicine and for lamp oil, is of a greenish tint, and a very little imparts its colour to a whole cask of coco-nut oil (Pharm. J. [3] 8, 363).

CALOTYPE v. PHOTOGRAPHY.

CALUMBA. Calumbæ radix, B.P.; Calumba, U.S.P. Colombo, Columbo. (Racine de Colombo, Fr.; Kalumba or Columbowurzel, Ger.)

The root of the Jateorrhiza Columba (Miers), a herbaceous climbing plant, inhabiting the forests of Eastern Africa (Flück. a. Hanb. 23; Bentl. a. Trim. 13). The fleshy root is sliced

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transversely and dried. It was introduced into Europe in the 17th century as an antidote for poison, and found a place in the London Pharmacopœia of 1788. It possesses mild bitter tonic properties, for which purpose it is now chiefly employed in medicine.

The drug contains 30–35 p.c. of starch, some mucilage, traces of a volatile oil, but no tannin; the root gives 4–7 p.c., the rhizome 12–17 p.c. of ash. There are further present two bitter principles and three alkaloids.

Columbin $C_{23}H_{22}O_9$ (according to Ulrich, Annalen, 1907, 351, 363; but cp. Feist, l.c.), the best-known bitter principle, occurs to the extent of 0·8 p.c., and is extracted by hot ether and recrystallised from the same solvent. It forms colourless prisms, m.p. 182°, hardly soluble in hot or cold water, little in cold alcohol or ether, readily in hot ether, chloroform, and alcohol. Columbin adds directly 8 bromine atoms. A crystalline diacetyl derivative melts at 218°. Boiling 5 p.c. potassium hydroxide yields columbic acid $C_{23}H_{32}O_{10}$, crystals, m.p. 220° (Frey, Annalen, 1907, 351, 372), boiling 15 p.c. hydrochloric acid gives an amorphous yellow substance and yellowish-green fluorescence. A second bitter principle, m.p. 246°, almost insoluble in most solvents, was isolated by Feist (Arch. Pharm. 1907, 245, 586).

The alkaloids were at first mistaken for berberine, to which they are closely related (Gordin, Arch. Pharm. 1902, 240, 146; Günzel, ibid. 1906, 244, 257; Gadamer, ibid. 1902, 240, 450; and particularly Feist, ibid. 1907, 245, 586) All three yield yellow quaternary salts. The aqueous solution of an alcoholic extract of the drug is extracted with ether to remove columbin (see above), and concentrated potassium iodide then precipitates the iodides, which are fractionally crystallised from alcohol. Columbamine iodide $C_{21}H_{22}N_9OI$, yellow needles, m.p. 224°, is the least soluble. Jateorrhizine iodide $C_{20}H_{20}O_5NI_3H_2O$ forms orange-yellow needles, m.p. 208°–210°; palmatine iodide $C_{9}H_{22}O_4NI$, slender yellow needles, m.p. 238°–240°. The first of these contains four methoxy

groups and one hydroxyl group ; it is a methyl ether of the second, which contains three methoxy and two hydroxyl groups, for methylcolumbamine and dimethyljateorrhizine are identical. Palmatine iodide contains four methoxyl groups, but no hydroxyl, anā hence remains undissolved on' treating the mixed iodides with sodium hydroxide. Its exact relationship to the other two is unknown. Reduction of the ·corresponding nitrates leads in all three cases to colourless tetrahydro derivatives. Methylcolumbamine is oxidised by permanganate to corydaldine (an oxydation product of corydaline, q.v.), a trimethoxy-o-phthalic acid (gallo-carboxylic acid ?), m.p. 200°, and a nitrogenous acid, ṁ.p. 200°-202°. The free bases corresponding to the above salts are unknown, so that it is doubtful whether the alkaloids are ammonium hydroxides or the corresponding anhydrides.

For the identification of columbin and the alkaloids under the microscope, see Tunmann, Pharm. Zentr H. 1914, 55, 775.   G. B

CALYCANTHINE $C_{11}H_{14}N_2$, crystals, m.p 243°-244° (dry), occurs with isocalycanthine, prisms, m.p. 235°-236° (dry), in the seeds of *Calycanthus glaucus* (Wild.), 2 p.c One nitrogen is secondary, the other tertiary. Toxic (Gordin, J. Amer. Chem. Soc. 1905, 27, 144, 1418 ; 1909, 31, 1305 ; 1911, 33, 1626).

CAMELINE OIL, *Dodder oil,* or *German Sesamé oil,* is prepared from the seeds of *Myagrum sativum* (Crz.), *Camelina sativa* (Linn), (' gold of pleasure ') Several centuries ago the seed was grown all over Germany as a crop, but at present it is only cultivated on a small scale in some part of South Germany, Belgium, Holland, Hungary, and the Balkan States, and South Russia. The seed is occasionally expressed in Hull, but, as a rule, the press cakes arrive in this country from Odessa, and are used (in Liverpool) in the manufacture of ' compound cakes.' The average composition of cameline seed is stated as follows :—

Oil	.	.	.	29·4 p c
Water	.	.	.	7·5 ,,
Proteins	.	.	.	25 9 ,,
Carbohydrates	.	.	.	17·3 ,,
Crude fibre	.	.	.	10·5 ,,
Ash	.	.	.	9·2 ,,

The oil has a golden-yellow colour and a pungent taste and smell. On exposure to the air it dries slowly. It is a semi-drying oil, and therefore yields, on boiling with litharge or manganese, a slowly drying varnish. The low saponification' value of the oil points to the presence of crucic acid

The ' cold-drawn ' oil is used for edible purposes in Russia. The oil expressed in this country, as also the oil expressed by heat in Hungary and the south of Russia, is used for soap making.

It has the following analytical characters : sp.gr. 0·9224-0·9260 at 15°; solidification point, —15°-19°; saponification value, 185-188 ; iodine value, 133-136 ; and m.p. of fatty acids, 18°-20°; molecular equivalent of fatty acids, 296. A sample examined by Grimme (Chem. Rev. Fett. Ind. 1912, 19, 102) contained 1 16 p.c. of unsaponifiable matter. According to van Ketel and Antusch (Zeitsch.

angew. Chem 1896, 581), linseed is liable to be contaminated with cameline seed, and so may yield an oil with a low iodine value.   J. L.

CAMPHOID. A preparation of one part of guncotton dissolved in 20 parts each of absolute alcohol and camphor.

CAMPEACHY WOOD *v.* LOGWOOD

CAMPHANIC ACID *v.* LACTONES.

CAMPHENE, CAMPHINE *v.* TERPENES.

CAMPHOL *v.* CAMPHORS.

CAMPHOPHORONE *v.* KETONES.

CAMPHOR. The term camphor was applied exclusively, in the sixth century, by Arabian and Chinese writers, to Borneo or Malayan Camphor (Borneol), but in the sixteenth century it included Laurel or Common Camphor, for Garcia d'Orta mentions the latter as well known in Europe in 1563, and points out what indeed is true at the present day, that the much more costly Borneo or Sumatra Camphor is entirely consumed in the East (cf. Fluck. a. Hanb. 510). The similarity in properties between laurel camphor and the crystalline separations from the volatile oils of plants, led, in the eighteenth century to an extension of the term camphor so as to include these solids. An attempt by Berzelius (Lehrbuch VI 580) to simplify the nomenclature, by calling all solid portions of volatile oils, ' stearoptenes,' and the liquid portions ' eleoptens ' has only resulted in the continued use, almost synonymously, of the words stearoptene and camphor. The discovery that laurel camphor contains oxygen has still further amplified the meaning of the word, which in its most comprehensive sense now includes most of the oxygenated products, both liquid and solid, of volatile oils.

Camphors are volatile oxygenated hydrocarbons, usually possessing a peculiar characteristic odour. They are mostly crystalline solids insoluble in water, but soluble in alcohol Except in the case of a few which are produced artificially they are obtained from plants where they occur associated with hydrocarbons from which they are probably derived. Most plants when distilled in steam yield volatile oils composed of heavier oxidised compounds held in solution more or less by lighter hydrocarbons. The former often separate in crystals during the condensation of the oil or afterwards on standing, or they may be obtained by fractional distillation.

The more important camphors, using the term in its larger signification, may be considered, for convenience, in 4 groups, as isomerides or homologues of : (1) Peppermint camphor, menthol $C_{10}H_{20}O$; (2) Borneo camphor, borneol $C_{10}H_{18}O$; (3) laurel camphor $C_{10}H_{16}O$; and (4) thyme camphor, thymol $C_{10}H_{14}O$. For the most part camphors behave like alcohols or phenols, but laurel camphor and menthone are ketones, cineol is an ether and alant camphor a lactone. The majority of camphors belong to saturated or unsaturated cyclic systems, but in 1891 Semmler (Ber. 24, 210) introduced the expression ' olefinic camphors ' for certain substances which possess an open chain structure, are closely related to the cyclic camphors, and are responsible for the aroma of many essential oils. The chief members of this group are citronellol $C_{10}H_{20}O$, geraniol, nerol and citronellal $C_{10}H_{18}O$, and citral $C_{10}H_{16}O$. (*See also* PERFUMES.)

Peppermint camphor. *Menthol* $C_{10}H_{19}OH$. 3-Me-6-*iso*propyl-1-cyclohexanol. The lævo modification of this camphor is the chief constituent of peppermint oil, the product of distillation of the herbs *Mentha piperita* (Linn.) and *M. arvei s* (Linn.), varieties *piperascev* and *glabraia*. It is also a minor constituent of a few of her volatile oils. A menthol of unrecorded rotatory sign predominates in the oil from *Hyptis suaveolens* (Linn.) (Bacon, Phillipine J. Sc. 1909, 4, A, 130). The proportion of menthol in normal Japanese oil of peppermint varies between 39 and 91 p.c., whilst English and American oils contain 48 to 68 p.c. A portion, about 10 p.c., of the menthol is present in ester form combined with acetic and *iso*valerianic acids. The camphor is extracted by freezing oils rich in menthol, whereby the crystals separate and are recovered either by pressure or by centrifugal treatment. The more important papers dealing with menthol in its bearing on oil of peppermint are: Beckett and Wright (Chem. Soc. Trans. 1876, 29, 1), Atkinson and Yoshida (*ibid* 1882, 41, 50), Moriya (*ibid*. 1881, 39, 77), Power and Kleber (Arch. Pharm. 1894, 232, '639), Power and Fluckiger (Pharm J. 1880 [3] 11, 220), Andres and Andreef (Ber 1892, 25, 609), and Schindelmeiser (Apoth. Zeit. 1906, 21, 927), and the semi-annual reports of Schimmel and Co., and of Roure Bertrand Fils.

Menthol crystallises in prisms belonging to the hexagonal system, and in appearance resembles magnesium sulph te It has a strong peppermint odour and taste, and produces a sensation of warmth on the tongue which is replaced by a sensation of cold when air is inhaled M p 42° 43 43·5°-44·5°, (Gildemeister and Hoffmann, Die Ätherischen Öle, 1910, i. 405), b p. 215·5° at 758 mm. (P. a. K.), sp gr 0 88 at 20° (Long, J. Amer. Chem. Soc. 1892, 14, 151), $[a]_D^{20} - 50·7°$ in 10 p.c. alcoholic solution (Beckmann, J. pr Chem. 1897, [2] 55, 15). Menthol is very slightly soluble in water, but soluble in the usual organic solvents and in concentrated hydrochloric acid. It rotates on the surface of water in a similar manner to laurel camphor. Mixed with chloral, thymol, or laurel camphor, menthol reacts forming a liquid (Kyle, Amer. J Pharm. 1885, 429 ; Becker, *ibid.* 1886, 283). When menthol is boiled with sulphuric acid diluted with half its volume of water it acquires an indigo-blue or ultramarine colour, the acid becoming brown (Brit. Pharm. 1914).

Menthol is a saturated secondary alcohol which under the influence of dehydrating agents, e.g. phosphorus pentoxide, zinc chloride, potassium bisulphate, passes into the hydrocarbon menthene, $C_{10}H_{18}$. A very large number of esters of menthol are known, of which the acetate $C_{10}H_{19}OAc$, b.p. 227°-228°, $[a]_D - 79·26°$, (cf. Kishner, J. Russ. Phys. Chem. Soc. 1895, 27, 480), and *isovalerianate*, $C_{10}H_{19}OOC \cdot C_4H_9$, occur in oil of peppermint (P. a. K.). For the identification of *l*-menthol by means of derivatives, the *phenylcarbamate* $C_{10}H_{19}OCONHPh$, m.p. 111° 112° (Leuckart, Ber. 1887, 20, 115), the *hydrogen phthalate* $C_{10}H_{19}OOC \cdot C_7H_5O_3$, m.p 122° (Pickard and Littlebury, Chem. Soc. Trans. 1912, 101, 118), and *benzoate* $C_{10}H_{19}OBz$, m.p. 55°-56° (P. a. L.) are characteristic.

Two atoms of hydrogen are removed from *l*-menthol by treatment with chromic acid mixture (Beckmann, Annalen, 1889, 250, 325) with formation of 1-*menthone*, a liquid ketone which occurs to the extent of about 20 p.c. in oil of peppermint (B. a. W.), and with an isomeride, d-*isomenthone*, forms 50 p.c. of American pennyroyal oil obtained from *Hedeoma pulegoides* (Linn.) (Barrowcliff, Chem. Soc. Trans. 1907, 91, 875). Menthol has been obtained synthetically from menthone and pulegone (Beckmann and Pleissner, Annalen, 1891, 262, 3?. Haller and Martine, Compt. rend. 1905, 140, 1209), also from thymol by use of the Sabatier and Senderens method of reduction. By this latter method the four possible menthols corresponding to menthone, namely, d- and l-menthol and d- and l-*neo*menthol, have been prepared (Pickard and Littlebury, Chem. Soc. Trans. 1912, 101, 110). A small proportion of d-*neo*menthol was isolated at the same time from Japanese oil of peppermint.

In its medicinal action menthol resembles phenol. Its chief uses are as a local anæsthetic for relief of superficial pains of various kinds, also dissolved in oil as a spray for influenza, hay fever, &c., and as a local application in certain cutaneous diseases.

Camphors isomeric with menthol. Citronellol $C_{10}H_{20}O$, a liquid isomeride of menthol occurs as *l*-citronellol in rose oil, *Rosa damascena* (Mill.) (Tiemann and Schmidt, Ber. 1896, 29, 922), and as d-citronellol in Java citronella oil, *Andropogon Nardus Java* de Jong (Schimmel's Rept. 1902, i. 14), and in the oil from *Barosma pulchella* (Linn.) (*ibid.* 1910, i. 17), whilst both forms occur in geranium oil, *Pelargonium graveolens* (Ait.) (Tiemann and Schmidt, Ber. 1896, 29, 924).

Borneo and Allied Camphors. *Malayan, Barus* or *Dryobalanops camphor* ; *Borneol, camphol* $C_{10}H_{17}OH$, 1, 7, 7,-trimethyl [1, 2, 2]-bicyclo 2-heptanol. This camphor occurs in nature in the dextro- and lævorotatory varieties, esterified chiefly in the lævorotatory modification. Common borneol, which is dextrorotatory, is the product of *Dryobalanops aromatica* (Gärtn.), a majestic tree indigenous to Sumatra, Borneo, and Labuan. The camphor is deposited in fissures in the old wood, and to obtain it the trees have to be sacrificed. The tree is cut down and the wood is examined by a laborious process of splitting. The collected camphor averages 7 to 11 lbs. from each tree. Owing to the reckless manner in which the trees have been destroyed without the planting of others, the forests of Sumatra now contain few that are worth working (Pharm. J. 1881, [3] 12, 83). The states of Sarawak and Brunei are much richer in trees, and at the present time produce borneol by similar methods (cf. Hanb. and Flück. 516 ; Kremers, Pharm Review, 1905, 23, 7 ; Gildemeister and Hoffmann, Die ätherischen Öle, 1916, iii. 178). The crude camphor is best purified by sublimation (Pelouze, Annalen, 1841, 40, 326).

d-Borneol is also a constituent of the following volatile oils: Rosemary, *Rosmarinus officinalis* (Linn.) (Gildemeister and Stephan, Arch. Pharm. 1897, 235, 586) ; Siam Cardamom *Amomum cardamomum* (Linn.) (Schimmel's Rept. 1897, ii. 9) ; Nutmeg, *Myristica fragrans* (Houtt.) (Power and Salway, Chem. Soc. Trans.

1907, 91, 2037); Lavender, *Lavandula vera* (D.C.) (Bruylants, J. Pharm. Chim. 1879, [4] 30, 139; *cf.* Charabot, Bull. Soc. Chim. 1897, [3] 17, 380); Spike Lavender, *Lavandula Spica* (Linn.) (Bouchardat, Compt. rend. 1893, 117, 53 and 1094), and Virginian Snake-root, *Aristolochia serpentaria* (Linn.) (Spica, Gazz, chim. ital. 1887, 17, 314). In addition to these natural sources *d*-borneol may be obtained, by the action of reducing agents on laurel camphor when borneol, of the same sign of rotation as the camphor used, is obtained mixed with a small proportion of *iso*borneol of opposite sign (Haller, Compt. rend. 1887, 105, 227; Beckmann, J. pr. Chem. 1897, [2] 55, 31), and in small proportion with *l*-borneol it is found among the products of the distillation of amber with potash (Berthelot and Buignet, Annalen, 1860, 115, 245).

Borneol is harder and less volatile than laurel camphor, and does not sublime in the bottles in which it is kept. It has a peppery camphoraceous odour and burning taste. M.p. 203°–204° (preparations containing *iso*borneol melt 206°–208°); b p. 212°, sp.gr. 1·011 (Plowman, Pharm. J. 1874, [3] 4, 711) It crystallises in the hexagonal system (Traube, J. pr. Chem. 1894, [2] 49, 3); $[a]_D + 37\cdot7°$ (Beckmann, Annalen, 1889, 250, 353; Haller, Compt rend. 1891, 112, 143; Pickard and Littlebury, Chem. Soc. Trans. 1907, 91, 1973). Borneol is a saturated secondary alcohol, and on oxidation yields *camphor*, $C_{10}H_{16}O$ of the same rotatory sign. Powerful oxidising agents produce *camphoric acid* $C_{10}H_{16}O_4$, and further degradation products (Laurent, Annalen, 1837, 22, 135; Pelouze, *ibid.* 1841, 40, 328; Kachler, *ibid.* 1878, 191, 143). Removal of a molecule of water by phosphoric anhydride gives rise to a solid terpene, *camphene*, $C_{10}H_{16}$ (Wallach, *ibid.* 1885, 230, 239); for the mechanism of this change, *see* Meerwein, *ibid.* 1914, 405, 129). Concentrated hydrochloric acid (Berthelot, *ibid* 1859, 112, 366), or phosphorus pentachloride (Kachler, *ibid.* 1879, 197, 89) reacts with borneol producing *bornyl chloride* $C_{10}H_{17}Cl$, a product identical with pinene hydrochloride or 'artificial camphor.' For the characterization of borneol the *phenylcarbamate*, $C_{10}H_{17}OCONHPh$, m.p. 138°–139° (Bertram and Walbaum, J. pr. Chem. 1894, [2] 49, 5), the *acetate* $C_{10}H_{17}OAc$, m.p. 29° (B. and W. Arch. Pharm. 1893, 231, 304), and the addition products with bromal, m.p. 105°–108° (Minguin, Compt. rend. 1893, 116, 889), and chloral, m.p. 55°–56° (Haller, *ibid.* 1891, 112, 145), are employed.

l-Borneol is a constituent of the following oils: Valerian, *Valeriana officinalis* (Linn.) (Bruylants, Ber. 1878, 11, 452; Oliviero, Bull, Soc. Chim. 1895, [3] 13, 917), Canadian Snake-root, *Asarum canadense* (Linn) (Power and Lees, Chem. Soc. Trans. 1902, 81, 63); Arbor vitæ, *Thuja occidentalis* (Linn.) (Wallach, Annalen, 1907, 353, 213), Citronella, *Andropogon nardus* (Linn.) (Schimmels, Rept. 1912, 1, 43), *Pinus maritima* (Mill.) (Belloni, Chem. Zentr. 1906, i. 1552), Yellow Pine, *Pinus palustris* (Mill.) (Schimmels, Rept. 1910, 1, 106), and Feverfew, *Matricaria Parthenium* (Linn.) (ibid. 1894, 1, 71). It is also contained in the fusel oil of the crude spirit obtained by the fermentation of the sugar of madder, and formerly known

as *madder camphor* (Jeanjean, Annalen, 1857, 101, 95), and in Ngai camphor, the name given to the solid part of the essential oil of *Blumea balsamifera* (D. C.) (Plowman, Pharm. J. 1874, [3] 4, 712; Flückiger, *ibid.* 828; Schimmels, Rept. 1910, 1, 149). From this latter source the *l*-borneol had a higher rotatory power $[a]_D$ −39° 25′, than is usually observed (Schimmels, Rept. 1895, 1, 74). On oxidation with nitric acid *l*-borneol yields laevorotatory camphor.

Numerous esters of borneol are known. Those of *l*-borneol, which occur in nature, are *bornyl acetate*, in oil of valerian (Bruylants), Siberian fir oil, *Abies sibirica*; Ledeb (Hirschsohn, Chem. Zentr. 1892, ii. 793), hemlock spruce oil, *Abies canadensis*; Michx. (Hunkel, Pharm Review, 1896, 14, 35), and coriander oil. *Coriandrum sativum* (Linn.) (Walbaum and Muller, Wallach Festchrift, 1909, 654), *borny formate, butyrate* and *isovalerianate* in oil of valerian (Bruylants).

Inactive borneol, the racemic mixture o *d*- and *l*-borneol has been obtained by the distillation of the crude product of the action of sulphuric acid on turpentine (Armstrong and Tilden, Chem. Soc. Trans. 1879, 35, 752); an ester of *i*-borneol is also obtained by treating pinene with oxalic acid (Schindelmeiser, J. Rus. Phys Chem. Soc. 1902, 34, 954).

*Iso*borneol, a stereoisomeride of borneol and an intermediate product in the manufacture of synthetic camphor, was first obtained by Bertram and Walbaum (J. pr. Chem. 1894, [2] 49, 1) from camphene obtained by the action of sodium acetate and glacial acetic acid on pinene hydrochloride at 200°. Camphene is warmed with glacial acetic acid and a little, 50 p.c., sulphuric acid, and the resulting acetate is decomposed by alcoholic potash. *Iso*borneol can now be prepared from pinene hydrochloride directly, by the action of boiling glacial acetic acid in the presence of a small quantity of a metallic salt such as anhydrous zinc chloride (Weizmann and Clayton Aniline Co., Eng. Pat. 8266, 1906). It is also formed to a small extent in the reduction of laurel camphor (Beckmann, J. pr. Chem. 1897, [2] 55, 35). It differs from borneol, physically, in its greater volatility, its higher m.p. 212° (in sealed tube), and its greater solubility in benzene and light petroleum, chemically in its greater stability towards oxidising agents, and in the ease with which it loses water forming camphene. Its bromal addition compound melts at 71°–72°. The optically active *iso*borneols melt at 214°, and have $[a]_D \pm 34\cdot3°$ (Pickard and Littlebury, Chem. Soc. Trans. 1907, 91, 1979).

Camphors isomeric with borneol. Cineol, Cajeputol or Eucalyptol $C_{10}H_{18}O$, anhydro 1-Me 4 (α-Me α-oxyethyl) 1-oxycyclohexane, is a constituent of a great number of volatile oils. It forms the major portion of the volatile oils of *Eucalyptus globulus* (Labill.) (Jahns, Ber. 1884, 17, 2941), Wormseed, *Artemisia maritima* (Linn.) var. *Stechmanni* (Wallach and Brass, Annalen) 1884, 225, 291, Hell and Sturcke, Ber. 1884, 17, 1970); Cajeput, *Melaleuca Cajeputi* (Roxb.) (Wallach and Gildemeister, *ibid.* 1888, 246, 276); *M. viridiflora* de Brogn. et Gris (Bertrand, Bull. Soc. Chim. 1893, [3] 9, 432). Cineol melts at 1°–1·5° (Schimmel & Co.); b.p. 176°

(Wallach, Annalen, 1888, 245, 195). It has a camphor-like odour and is optically inactive. It is characterised by its addition compounds, with the halogens, with hydrobromic acid, m.p. 56°, which also serves for the isolation of small quantities (Wallach, Annalen, 1888, 246, 280), with phosphoric acid (Scammell, D. R. P. 80118), with arsenic acid (U.S. Pat. 705545, Thoms and Molle, Arch. Pharm. 1904, 242, 172), with iodole (tetraiodopyrrol), m.p. 112° (Bertram and Walbaum, Arch Pharm. 1897, 235, 178), by means of which very small quantities can be detected (Hirschsohn, Chem. Zentr. 1893, i 503, and with resorcinol (Baeyer and Villiger, Ber. 1902, 35, 1209). The compounds with hydrobromic acid, phosphoric acid, arsenic acid, and resorcinol are used for its quantitative estimation (cf. Turner and Holmes, Amer. J. Pharm. 1915, 87, 101), the question as to their relative efficiency being still a matter of dispute. Dehydrating agents convert cineol into dipentene $C_{10}H_{16}$ (Wallach and Brass; Hell and Sturcke; Oxidation by permanganate gives cineolic acid $C_{10}H_{16}O_5$, m.p. 197 (Wallach and Gildemeister), but towards reducing agents it is very stable. The oxygen atom in cineol is present as an oxide or ether linking. The artificial production of cineol has been effected by the action of dilute acids on terpineol or terpin hydrate (Wallach, Annalen, 1887 239, 18).

Cineol is used in medicine as a local antiseptic dressing, and for catarrhal conditions of the respiratory mucous membranes.

The volatile oils of the following contain other isomerides of borneol ; Citronella, Andropogon Nardus (Linn.) (Semmler, Ber. 1893, 26, 2254) and Eucalyptus citriodora (Hook.) (Schimmels, Rept 1907, 2, 35) contain d-Citronellal, whilst l-Citronellal is contained in ' Java lemon oil ' (ibid. 1903, I, 21). Linalool, Ocotea caudata (Mez.) (Barbier, Compt. rend. 1895, 121, 168), Lavender, Lavandula vera (D.C.) (Bertram and Walbaum, J. pr. Chem. 1892, [2] 45, 590) ; Bergamot, Citrus Aurantium (Linn.) (Bertram and Walbaum, ibid. 602) contain l-linalol ; whilst d-linalol (' coriandrol ') is contained in oil of coriander, Coriandrum sativum (Linn.) (Barbier, Compt. rend. 1893, 116, 1460). Geranium, Pelargonium graveolens (Ait.) (Bertram and Gildemeister, J. pr. Chem. 1894, [2] 49, 191), Citronella, Andropogon Nardus (Linn.) (Schimmels, Rept. 1893, 2, 12); Lemon grass, Cymbopogon flexuosus (Stapf.) (Tiemann and Semmler Ber. 1893, 26, 2721) contain geraniol (' rhodinol '). Neroli oil from Citrus Aurantium (Linn.), subspec. amara (Linn.) (Hesse and Zeitschel, J. pr. Chem. 1902, [2] 60, 481) contains nerol. d-a-Terpineol, m.p. 37°-38°, is a constituent of oil of sweet orange, Citrus Aurantium (var.) dulce (Linn.) (Stephan, J. pr. Chem. 1900, [2] 62, 523) of neroli and petit-grain oils ; l-a-terpineol of oil of camphor, Cinnamomum Camphora (Nees et Eberm.) (Schimmels, Rept. 1903, 2, 39) ; i-Terpineol, m.p. 35°, of cajeput oil, Melaleuca cajeputi (Roxb.) (Voiry, Bull. Soc. Chim. 1888, [2] 50, 108).

Common and allied camphors. Laurel Camphor ; Dextro Camphor. (Camphre, Fr. ; Campher, Ger.) $C_{10}H_{16}O$ 1.7.7-Trimethyl s[1-2.2]-bicyclo 2-heptanone. Common camphor is contained in all parts of the camphor la rel, Ci innamomum

Camphora (Nees et Eberm.), a tree inhabiting Japan, Formosa and Southern China. It occurs also as a constituent of the volatile oils of Spike, Lavandula spica (D.C.) (Lallemand, Annalen, 1860, 114, 198); Rosemary, Rosmarinus officinalis (Linn.) (ibid. 197) ; Sage, Salvia officinalis (Linn.) (Muir, Chem. Soc. Trans. 1880, 37, 678) ; Siam Cardamom, Amomum Cardamomum (Linn.) (Schimmels, Rept. 1897, 2, 9) ; American Wormseed, Chenopodium ambrosoides (Linn.) var. anthelminthicum (Gray) (ibid. 1908, 1, 112), and Sassafras, Sassafras officinalis (Nees) (Power and Kleber, Pharm. Review, 1896, 14, 101).

Although camphor is at the present time still manufactured artificially, most of the camphor of commerce is obtained from the camphor laurel, the chief industry being confined to Japan, Formosa and China. The experimental plantations which were undertaken for the production of natural camphor in Florida, California, Jamaica, East Africa, Malay States, Algeria and Ceylon have at least in one case, that of Florida, begun to furnish camphor on the commercial scale (Oil, Paint and Drug Rep., March 29, 1915). In Formosa the camphor industry before the China-Japanese war was nominally in the hands of the Chinese, but owing to the savage state of the interior of the island, and the unscrupulous methods of the dealers, it had declined to small and unimportant proportions. Afterwards Japan assumed the control of the industry, and it was made a government monopoly in 1899, and this was extended to Japanese camphor in 1903. Since the establishment of the monopoly the old crude methods of obtaining the camphor (Fluck. and Hanb. 513) have been replaced by more modern ones. The camphor wood in the form of chips is steamed in roughly built furnaces, and the camphor which is driven off is condensed in cooled wooden vessels, and freed from most of the oil by draining, crude or ' grade B ' camphor being thus obtained. For the production of refined or ' grade A ' camphor, the crude material is heated in large iron retorts, through which a current of air is passed. For the first 48 hours only sufficient heat is applied to drive off the water and oil. The retorts are then connected with a condensing chamber, the roof of which is cooled by running water, and are heated to a high temperature in order to volatilise the camphor. It is then formed into blocks in wooden moulds and pressed, first by steam power and finally by a very high hydraulic pressure (Collins, J. Soc. Chem. Ind. 1904, 75). The yield of camphor is greater in winter than in summer, while the reverse is true of the oil. In summer a charge of 120 kilos. of wood gives 2·4 kilos., or 2 p.c. of camphor, and 1·8 litres of oil ; in winter, 3 kilos., or 2·4 p.c. of camphor and 0·5-0·7 litre of oil.

Crude camphor appears in commerce as a coarse wet powder of a greyish-white colour. Chinese crude camphor is packed in round wooden pots of about 150 lbs. net content, Japanese in lead-lined wooden boxes containing about 130 lbs. net. The principal impurities of crude camphor are water, camphor oil, iron, sand, wood, &c. Light oil of camphor has a sp.gr. of 0·895-0·920; b.p. 170°-180°, and contains pinene, camphene, dipentene, phellandrene and

fenchene. *Heavy oil of camphor*, having a sp.gr. of 0·960–0·970, and b.p. 240°–300°, contains cadinene, safrol, eugenol, cineol, fenchone, terpineol, &c. Besides these compounds, both of the oils contain a large amount of camphor in solution. Before refining crude camphor, the oil and water must be got rid of, as the oil gives the refined camphor a fatty touch, and the water renders it opaque. The elimination of water and oil is often effected by washing in a centrifugal machine with small quantities of water; the liquid draining off contains both oil and water. The separation is also done by hydraulic pressure, or by crystallisation from boiling benzene or light petroleum. Resublimation in Europe is done principally in glass retorts, yielding a round concave cake weighing 6–8 lbs., having an opening in the centre. In America the camphor is sublimed from flat iron pans with non covers, yielding plates of about 18 inches square and 1 inch thick, weighing from 8 to 10 lbs. The process consists in mixing the camphor with a little lime, charcoal or iron filings, according to the quality, and charging each pan with about 12 lbs. of material; the subliming pans are heated slowly for 2 hours, and then fired rapidly up to 190°, this temperature being kept for from 12 to 16 hours. After cooling, the refined product is removed from the cover by slightly heating, and is then cut into the desired shape (Drobegg, J. Soc. Chem. Ind. 1907, 381).

Purified camphor comes on to the market in three forms, 'bells,' 'blocks' and 'flowers.' Block camphor consists of colourless translucent masses traversed by numerous cracks. It can be broken but is too tough to admit of being powdered by trituration. This may, however, be readily effected if a little alcohol be added, which escapes again during the operation. Camphor finds very extensive commercial application in the preparation of celluloid, in medicine where it is used externally as a mild rubefacient and to destroy parasites, internally, as a carminative and intestinal disinfectant, and to a minor extent in the manufacture of explosives. Sp.gr. 0·986–0·996; m.p. 175°, 178·75° corr. (Lenz. Arch Pharm. 1911, 249, 289); b.p. 204°. It sublimes to some extent at ordinary temperatures and condenses in hexagonal crystals (cf. Folger, Y.B. Pharm. 1886, 232); [α]_D 44·22° in 20 p.c. alcoholic solution (Beckmann, Annalen, 1889, 250, 353). Refraction coefficient (Kanonnikof, J. pr. Chem. 1885, [2] 31, 348). Camphor in common with chloral hydrate and some other substances rotates in a peculiar manner on the surface of water (lowering of surface tension by solution), (Tomlinson, Phil. Mag 1873, [4] 46, 376; Pharm. J. 1874, [3] 4, 654, 672; Chem. News, 1885, 52, 50). It is very sparingly soluble in water (1 : 700), readily in 90 p.c. alcohol (1 : 1), also in chloroform and ether. Mixed with chloral hydrate, it forms an oily liquid $C_{10}H_{16}O$, CCl_3CHO,H_2O, which has been employed in medicine as an anodyne pigment (Brown, Pharm. J. 1873, [3] 4, 729; Saunders, *ibid.* 1376, [3] 7, 89; Cazeneuve and Imbert, Bull. Soc. Chim. 1880, [2] 34, 209; Zeidler, J. 1878, 645; Albright, Amer. J. Pharm. 1886, 282). Similar combinations take place between camphor and chloral alcoholate (Zeidler), phenol,

(Léger, Bull Soc. Chim. 1890, [3] 4, 725); menthol (Kylo, Amer. J. Pharm. 1885, 429), and thymol (Symes, Pharm. J 1879, [3] 9, 598).

Camphor is a saturated hydroaromatic ketone, but does not combine with sodium bisulphite. For identification purposes use is made of the *oxime* $C_{10}H_{16}NOH$, m.p. 118°–119° (Auwers, Ber. 1889, 22, 605), the *semicarbazone* $C_{10}H_{16}=N\cdot NHCONH_2$, m.p. 236°–238° (Tiemann, Ber. 1895, 28, 2191), the *oxymethylene compound* $C_{10}H_{14}O=CHOH$, m.p. 80°–81°, and the *benzylidene compound* $C_{10}H_{14}O=CHC_6H_5$, m.p. 96°. Of its substitution products, one, *α-bromocamphor* $C_{10}H_{15}OBr$ has been employed in medicine as a sedative in nervous excitement, and is an article of trade. It is best prepared by treating powdered camphor with bromine at 100°, pouring the liquefied product into water and recrystallising from spirit (Armstrong and Matthews, Chem News, 1878, 37, 4) It has a weak camphoraceous odour and taste; m p 76°; b.p. 274°. It is insoluble in water, but soluble in the common organic solvents, in fixed oils, and in sulphuric acid By the action of reducing agents camphor is converted into a mixture of borneol and *isoborneol*, the former predominating (Beckmann, J. pr. Chem. 1897, [2] 55, 35; Haller, Compt rend 1887, 105, 227). On oxidation with nitric acid (Kaehler, Annalen, 1878, 191, 143) or hot alkaline permanganate (Grosser, Ber. 1881, 14, 2507), camphor yields *camphoric acid* $C_8H_{14}(COOH)_2$.

Synthetic Camphor; Inactive Camphor. Camphor can be manufactured from turpentine oil, and has from time to time appeared on the market. It is termed 'synthetic' camphor to distinguish it from the so-called 'artificial camphor,' which consists of pinene hydrochloride, and is unsuitable for the chief purposes to which camphor is applied. Only when the prices of the natural product are abnormally high has synthetic camphor been able to compete with it. During the war, in Germany, owing to the failure of supplies of *d*-camphor, the Schering interests and probably other firms (Houseman, Amer. J. Pharm. 1915, 87, 58) produced synthetic camphor in quantity, whilst the American Camphor Corporation contend that they can supply the requirements of the celluloid trade with synthetic camphor (Oil, Paint and Drug Rep., March 29, 1915). Natural camphor and synthetic camphor only differ in their action on polarised light, the latter being either inactive or showing only a slight activity; in their physiological action they are identical (Joachimoglu, Ber. deut. Pharm. Ges. 1916, 26, 427). By working at low temperatures, however, Darmois (Compt rend. 1910, 150, 925) has obtained synthetic camphor with the rotation of natural camphor, French oil of turpentine yielding *l*-camphor, whilst turpentine from the Aleppo pine, *Pinus halepensis* (Mill.) yielded *d*-camphor. The various routes taken by patented processes for the manufacture of synthetic camphor are shown by Fig. 1.

The first commercial process consisted essentially in converting oil of turpentine into pinene hydrochloride, which compound by elimination of hydrogen chloride yields camphene. Camphene is then converted into *isoborneol*, which, like natural borneol, yields camphor on oxidation. For the preparation of pinene

hydrochloride, oil of turpentine, which contains 70-90 p.c. of pinene, depending on its origin, is treated with dry hydrogen chloride, whereby a solid hydrochloride is obtained together with a
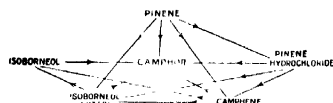

Fig 1.

liquid hydrochloride which is not suitable for the manufacture of camphene. This liquid hydrochloride contains a considerable proportion of the solid hydrochloride in solution, which may be recovered by oxidising the oily product with dilute nitric acid, or by extraction with petroleum after treatment with sulphuric acid at 40°, which polymerises the oil (Eng. Pat. 7319, 1908). The preparation of camphene by the removal of hydrogen chloride from pinene hydrochloride (Wallach, Annalen, 1887, 239, 6 ; Bruhl, Ber. 1892, 25, 147 ; Reychler, Bull. Soc. Chim. 1896, [3] 15, 371) was at first attended with difficulty : the yield was small and the product was liable to contain chloride. During the last two decades the following methods have been patented for the production of camphene in large quantities, many of which are claimed to give almost theoretical yields and a product free from chloride. Heating the hydrochloride with bases of the aliphatic series such as methylamine, or with piperazine or piperidine (U.S. Pat. 757270, 1902), or with tertiary bases of the pyridine and quinoline group (Eng. Pat. 5032, 1906) ; by heating with alcoholic, aqueous, or gaseous ammonia (U S Pat. 707271, 1902), or ammonia in presence of a phenol (D. R. P. 264246, 1912) ; by heating with aqueous sodium hydroxide or ammonia in presence of a soap (U.S. Pat. 725890, 1903) ; by heating with lead acetate in glacial acetic acid solution (Fr. Pat. 349896, 1904) ; by heating with glacial phosphoric acid in glacial acetic acid solution (D. R. P. 207888, 1908) ; by heating with a metallic salt of a higher fatty acid (Eng. Pat. 19960, 1906 ; 1948, 1907), or with a mixture of metallic salts of the fatty acids (Eng. Pat. 2488, 1913) ; by heating with a metal and an oxidising agent, such as zinc and barium peroxide in molecular proportions (Fr. Pat. 361333, 1905) ; by heating with salts of phenols or naphthols either anhydrous or in presence of water (Eng Pat. 16429, 1906 ; 21180, 1906 ; 5674, 1908) ; by heating with lime or other similar oxide (Fr. Pat. 575897, 1907 ; Eng. Pat. 25453, 1907), in the presence of phenol at 180° (Eng. Pat. 22810, 1906), in the presence of polyvalent alcohols or carbohydrates (Eng. Pat. 10784, 1907) ; by heating with alkali, and alkali or alkaline earth salt of a sulphonic acid of the benzene or naphthalene series (Eng. Pat. 10783, 1907) ; by heating with alkali or alkaline earth salts of organic sulphamides or with phenolsulphonic acids (D. R. P. 107340, 107805, 1907) ; by heating with alkali or alkaline earth hydroxides in presence of compounds which combine with water such as alkali or alkaline earth oxides (Fr. Pat. 413282, 1909) ; by heating with zinc oxide in presence of alkali hydroxide (Eng. Pat. 11029, 1911) ; by

heating with α- or β-naphthylamine (D, R. P. 206386, 1907), or with aniline (D. R. P. 205850, 1907) ; by heating with a meta- or pyro-borate, silicate, phosphate or arsenate in aqueous solution (D. R. P. 205295, 1908) ; by heating with phenol, cresol or naphthol and the carbonate of an alkali or alkaline earth metal (Eng. Pat. 13902, 1909) ; by heating under reflux until the hydrochloric acid has gone (U.S. Pat. 923967, 1909) ; by the Grignard reaction (Hesse, Ber. 1906, 39, 1127). According to Eng. Pat. 10227, 1910, pinene vapour when passed over a catalyst at 200°–300° is converted into camphene.

Bertram and Walbaum (J. pr. Chem. 1894, [2] 49, 1) made the discovery that camphene is converted into isoborneol by warming with a mixture of acetic acid and a little sulphuric acid, and decomposing the resulting isobornyl acetate by alcoholic potash. This method is employed on the manufacturing scale. A variant of the method is described in Eng. Pat. 19961, 1906, where camphene is heated with oxalic acid in a suitable solvent with a condensing agent such as sulphuric or phosphoric acids with formation of normal and acid esters of isoborneol. Camphene has also been directly converted into isoborneol by boiling in acetone with half its weight of 20 p.c. H_2SO_4 for 10 hours, or in an autoclave at 100° for a shorter time (Fr. Pat. 385341, 1907). The isoborneol purified by crystallisation from light petroleum or benzene is then oxidised to camphor. For this purpose various oxidising agents are employed, many of which have been patented. Amongst these are : potassium permanganate in glacial acetic acid (Ber. 1900, 33, 3430) ; aqueous solution of permanganate employed with a benzene solution of isoborneol (Fr. Pat. 341513, 1904) ; potassium permanganate in alkaline solution (D. R. P. Anm. 38311, 1904) ; chlorine, either gaseous or in solution (Eng. Pat. 28035, 1904 ; U.S. Pat. 802792, 1905) ; hypochlorite, either alone (U.S. Pat. 804162, 1907), or in presence of copper and ferric chlorides (Eng. Pat. 20050, 1908) ; chromic acid or chromates (Eng. Pat. 26779, 1904 ; 14550, 1907) ; in acetone solution (Eng. Pat. 21946, 1907) ; or in presence of an indifferent solvent (Eng. Pat. 5513, 1908 ; 24779, 1912) ; nitric acid in which the presence of nitrous acid is essential (Eng. Pat. 9857, 1907) ; nitric acid in presence of vanadic acid and oxygen (Eng. Pat. 18047, 1908) ; nitric acid in presence of a halogen (U.S. Pat. 1313661, 1919) ; oxygen (U.S. Pat. 801405, 1905) ; oxygen, oxides of heavy metals or peroxides (Fr. Pat. 385352, 1907) ; basic oxidising substances, e.g. CuO, HgO (Eng. Pat. 3750, 1908) ; metals or oxides which can liberate hydrogen from isoborneol (Eng. Pat. 26708, 1908) ; electrolytic methods (U.S. Pat. 875062, 1907 ; Fr. Pat. 387539, 1907) ; ozone (U.S. Pat. 801483, 1905) ; nitrous anhydride (U.S. Pat. 802793, 1905) ; metallic copper at 300° in absence of air (Eng. Pat. 17573, 1906). According to U.S. Pat. 790601, 1905, and Eng. Pat. 21171, 1906, isobornyl acetate and other isobornyl esters can be directly oxidised to camphor without previous saponification.

Camphene can also be directly oxidised to camphor (Armstrong and Tilden, Ber. 1879, 12, 1756), and the following processes have been patented : Treatment with ozone at 80° (Eng. Pat 21294, 1890) ; treatment with hot air or

oxygen (Eng. Pat. 3555, 1896) ; oxidation by potassium permanganate in acetone solution (addition to Fr. Pat. 349896, 1904) ; treatment of camphene at 180° with an oxidising agent, such as chromic acid, converts it into oxonide $C_{10}H_{16}O_3$, which loses oxygen on treatment with water, and is converted into a lactone, camphenolide, which yields camphor on heating in presence of water (Fr. Pat. 361333, 1905) ; oxidation with a per- salt of potassium and sulphuric acid (Fr. Pat. 389092, 1908).

Another method of obtaining synthetic camphor depends on the formation of bornyl and isobornyl esters by the direct action of various acids on pinene or turpentine oil. The following processes have been patented : Treatment of anhydrous turpentine at 120°-130° with anhydrous oxalic acid (U.S. Pat. 698761, 1902, cf. Pond, J. Soc. Chem. Ind. 1907, 385) ; by heating pinene with anhydrous oxalic acid in presence of anhydrous chlorides, e.g. $AlCl_3$ with the addition of a diluent (Eng. Pat. 14408, 1908) ; by heating turpentine with an alcohol and an acid anhydride, e.g. B_2O_3 at 120°-140° (Eng. Pat. 11248, 1908) ; by heating pinene with an aromatic polysubstituted acid (Eng. Pat. 18049, 1908) ; terpenes or oils containing terpenes heated at 160° with propionic or butyric acid (Fr. Pat. 408106, 1909). Similar methods, based on the direct formation of bornyl or isobornyl esters from pinene hydrochloride, have been patented : by heating with an alkaline formate or oxalate in alcohol and water for 10 hours to 120° (Eng. Pat. 5549, 1904) ; by heating with metallic formates and formic acid (Eng. Pat. 14379, 1907) ; solid pinene hydrochloride is heated with an alkaline earth oxide in presence of excess of a lower member of the fatty acids (Fr. Pat. 393504, 1908) ; turpentine treated with dry hydrochloric acid gas is boiled with an alkali, alkaline earth or metallic butyrate or propionate in presence of excess of the corresponding fatty acid (Fr. Pat. 408065, 1909) ; by heating pinene hydrochloride in acetic acid solution with lead acetate (Fr. Pat. 349896 1904) ; by heating in acetic acid solution with an acetate and fused $CaCl_2$ or $KHSO_4$ (Eng. Pat. 1936, 1908) ; by heating with acetic acid in presence of zinc chloride (Eng. Pat. 8266, 1906), or some other zinc salt (Eng. Pat. 10798, 1906), and with addition of an alkali or alkaline earth salt of a formate, acetate or butyrate (Eng. Pat. 18280, 1906) ; by heating with the acetate of an alkaline earth for 20 hours at 180° (Fr. Pat. 375590, 1907) ; by heating with a fatty acid in presence of metallic zinc (Eng. Pat. 16605, 1907), or by heating with organic acids in presence of zinc (Eng. Pat. 14752, 1908) ; by heating with fatty acids and zinc chloride in presence of cobaltous chloride or other suitable inorganic salt (Eng. Pat. 22129, 1907) ; solid pinene hydrochloride is shaken with a salt of acetic or stearic acid or phenol with an excess of either acetic, stearic acid or phenol in presence of a dehydrant (Fr. Pat. 382790, 1906).

The direct conversion of pinene hydrochloride into camphor is claimed in Eng. Pat. 27317, 1913, by heating with nitric acid or its salts in presence of a catalyst, whilst two processes for the conversion of turpentine into camphor have been patented. They are : turpentine is treated with a halogen at a low

temperature, -25°, until the increase in weight is 25-50 p.c., and the product, still at a low temperature, is mixed with one-eighth to one-fifth its weight of NaOH, when it is converted into camphor (Fr. Pat. 392182, 1907) ; turpentine in a neutral solvent is treated with nascent oxygen (Fr. Pat. 406005, 1908).

(For analyses and points of difference between natural and commercial synthetic camphor, see Crane and Joyce (J. Soc. Chem. Ind. 1907, 386), Lohmann (Ber. deut. Pharm. Ges. 1909, 19, 222), and Lenz (Arch. Pharm. 1911, 249, 289).)

Lævo camphor ; *Matricaria camphor.* This camphor occurs naturally in the volatile oils of Feverfew, *Matricaria Parthenium* (Linn.) (Chautard, J. pr. Chem. 1848, 45, 45 ; Compt. rend. 1853, 37, 166) ; Tansy, *Tanacetum vulgare* (Linn.) (Schimmels, Rep. 1895, ii. 35) ; and *Artemisia Nana* (Pursh.) (Whittelsey, Chem Zentr. 1909, ii. 2160). It is also a constituent of Ngai camphor, the solid portion of the oil of *Blumea balsamifera* (D.C.) (Schimmels Rep 1910, i. 149). It can be prepared by oxidation of camphene obtained from lævorotatory pinene (Riban, Bull. Soc. Chim. 1900, 24, 19 ; Darmois, Compt. rend. 1910, 150, 925), and by oxidation of *l*-borneol with nitric acid (Pope and Harvey, Chem. Soc. Trans. 1901, 79, 76). It differs from common camphor only in its behaviour towards polarised light.

Inactive camphor is a constituent of the oil of *Chrysanthemum sinense* (var.) *japonicum* (Keimatsu, J. pharm. Soc. Japan, 1909, 236, 1).

The following are the more important isomerides of camphor which occur naturally in volatile oils : *Pulegone* $C_{10}H_{16}O$, is only found in oils of the *Labiatæ*, chiefly in European Pennyroyal, *Mentha pulegium* (Linn.) (Beckmann and Pleissner, Annalen, 1891, 262, 1) ; *Fenchone* in its *dextro* modification is a constituent of oil of Fennel, *Foeniculum vulgare* (G.) (Wallach, Annalen, 1891, 263, 129), whilst the *lævo* variety is found in oil of Thuja, *Thuja occidentalis* (Linn.) (Wallach, Annalen, 1892, 272, 99) ; *Thujone* occurs in three forms, as d-*a-thujone* in Thuja oil (Paolini and Divizia, Atti. R. Accad. dei Lincei, 1912, 21, [1] 570) ; as l-*a-thujone* in the same oil (Wallach, Annalen, 1893, 272, 99) ; and as d-β-*thujone* in oil of Tansy, *Tanacetum vulgare* (Linn.) (Semmler, Ber. 1892, 25, 3343), and oil of Wormwood *Artemisia Absinthium* (Linn.) (ibid.) ; *Citral* is a frequent constituent of volatile oils and a major ingredient of the oil from *Backhousia citriodora* (F. v. M.) (Bertram, Schimmels, Rep. 1888, ii. 17), and of Lemon-grass oil, *Cymbopogon flexuosus* (Stapf.) (ibid.) ; *Sabinol* is the most important constituent of oil of Savin, *Juniperus Sabina* (Linn.) (Fromm, Ber. 1898, 31, 2025).

The more important homologues of common camphor belong to the sesquiterpene alcohols (*see* TERPENES). Owing to their capacity for crystallising from volatile oils some of them have long been known.

Matico camphor $C_{15}H_{26}O$, was formerly a constituent of oil of matico, *Piper angustifolium* (Ruiz et Pavon), but appears to be absent from present day oils. M.p. 94°, $[a]_D - 28.7°$ (in chloroform). Boiling with 25 p.c. sulphuric acid converts it into a blue sesquiterpene

$C_{15}H_{24}$ (Kügler, Ber. 1883, 16, 2841 ; Thoms, Arbeit. Pharm. Inst. Berlin, 1905, 2, 125).

Cedar camphor, Cypress camphor, Cedrol $C_{15}H_{26}O$, is a frequent constituent of the volatile oil of *Juniperus virginiana* (Linn.), m.p. 86°-87°, $[a]_D$ 9.5 (in alcohol). It yields cedrene $C_{15}H_{24}$ when treated with phosphoric anhydride (Walter, Annalen, 1841, 39, 247, *cf.* also Semmler and Mayer, Ber. 1912, 45, 1384).

Cubebs camphor $C_{15}H_{26}O$, is a constituent of the volatile oil of *Piper Cubeba* (Linn.), when it has been exposed to the air for some time. M.p. 68°-70°, b.p. 148°, with loss of water, a change which very readily takes place under various conditions of treatment forming a sesquiterpene (Schmidt, Ber. 1877, 10, 188 ; Schaer and Wyss, Arch. Pharm. 1875, 206, 316).

Ledum camphor $C_{15}H_{26}O$, obtained from the volatile oil of Marsh Tea, *Ledum palustre* (Linn.). Needles, m.p. 104°-105°, b.p. 282°-283°. The sesquiterpene, *ledene* $C_{15}H_{24}$, is readily produced by the action of dehydrating agents (Rizza Chem. Zentr. 1887, 1257 ; Hjelt, Ber. 1895, 28, 3087 ; Loundse, Chem. Zeit. Repert, 1903, 27, 284).

Patchouli camphor, patchouli alcohol $C_{15}H_{26}O$, crystallises out from patchouli oil, the product of *Pogostemon Patchouli* (Pell.), m.p. 56°, $[a]_D$ —97.7° (in chloroform). It readily loses the elements of water forming *patchoulene* $C_{15}H_{24}$ (Montgolfier, Compt. rend. 1877, 84, 88 ; Wallach, Annalen, 1894, 279, 394 Schimmel, Rep. 1905, 1. 62).

Eudesmol $C_{15}H_{26}O$ is a constituent of the oils of various species of *Eucalyptus*, but especially of *E. macrorhyncha* (F. v. M.) (Baker and Smith, J. Linn. Soc. N.S.W. 1899, 33, 86) M.p. 84°, $[a]_D$ 31.3° (in chloroform) (Semmler and Tobias ; Ber. 1913, 46, 2026 ; Semmler and Risse, *ibid.* 2303).

Thyme and allied camphors. *Thymol* $C_{10}H_{14}O$, *Isopropyl m*-cresol

Thymol is a constituent of the volatile oils of Ajowan, *Carum copticum* (Benth.) (Haines, Chem. Soc Trans. 1856, 8, 289 ; Stenhouse, Annalen, 1855, 93, 269 ; *ibid.* 1856, 98, 309 ; Muller, Ber. 1869, 2, 130) ; Thyme, *Thymus vulgaris* (Linn) (D. Peri, Annalen, 1848, 64, 374 ; Lallemand, *ibid.* 1857, 102, 119) ; Wild Thyme, *T. Serpyllum* (Linn.) (Jahns, Ber. 1882, 15, 819, *Ocimum viride* (Willd.) (Goulding and Pelly, Proc. Chem. Soc. 1908, 24, 63) ; Horsemint, *Monarda punctata* (Linn.) (Arppe, Annalen, 1846, 58, 41) ; *Satureia Thymbra* (Linn.) (Schimmels, Rep. 1889, ii.55) ; *Origanum hirtum*, (Link.) (Holmes and Umney, Perf. and Essent. Oil Rec , 1913, 4, 73). On the manufacturing scale it is prepared from Ajowan and Horsemint Oils (*cf.* Holmes, Perf. and Essent, Oil Rec., 1916, 7, 311 ; also U.S. Dept. Agric. Bull. 372, 1916), by extraction with caustic soda solution, when the thymol forms a water soluble sodium salt, and is thus separated from the hydrocarbons. The alkaline solution is acidified with hydrochloric acid, which precipitates the crude camphor. It may then be purified by crystallisation from glacial acetic acid or alcohol. Another plan is to submit the oil to fractional distillation and to freeze out the thymol from the heavier portions of the distillate. A possible source for syn-

thetic thymol is cymene (U.S. Pat. 1306512, 1919).

Thymol has the odour of thyme and a warm pungent taste ; m.p. 50.5°-51.5° ; b.p. 232° at 752 mm. It is sparingly soluble in water (1 : 1200) and glycerine (1 : 1000), but readily in the usual organic solvents and alkaline solutions. It forms a liquid with menthol (Kyle, Amer. J. Pharm. 1885, 429) ; camphor (Symes, Pharm. J. 1879, [3] 9, 598) ; berberine (Lloyd, New Remedies, 1881, 195) ; But not with chloral hydrate (Symes, *cf.* Mazzara, Gazz. chim. ital. 1883, 13, 272). If a solution containing thymol be warmed with half its volume of glacial acetic acid, together with more than its volume of sulphuric acid, a deep red-violet colour is developed. This reaction is obtained even in very dilute solutions. For the further identification of thymol use is made of the *phenyl carbamate* $C_{10}H_{13}OCONHPh$, m.p. 107° (McKenzie and Semmler, Ber. 1906, 39, 1158), and *nitrosothymol* $C_{10}H_{13}O(NO)$, m.p. 160°-162° (Schiff, Ber. 1875, 8, 1500). The *methyl ether* of *thymol* $C_{10}H_{13}OMe$ occurs naturally in the essential oil of sea-samphire, *Crithmum maritimum* (Linn.) (Delépine and Belsunce, Bull. Soc. Chim. 1918 [iv.] 23, 24).

For estimation of thymol in essential oils, Kremers and Schreiner (Chem. Zentr. 1897, ii. 147, *cf.* Messinger and Vortmann, Ber. 1890, 23, 2753) recommend the following process : A known weight of the sample is mixed with an equal volume of light petroleum in a stoppered burette, and agitated with 5 p.c. aqueous caustic soda till no further diminution of the oily layer takes place, and a drop of the oil dissolved in 20 drops of chloroform, on gently warming with a small piece of sodium hydroxide, does not turn red. The decrease in volume is observed or the alkaline liquor can be titrated with iodine, but it appears the results obtained by titration are about 3 p.c. lower. (For iodometric estimation, *see* also Messinger (J. pr. Chem. 1900, [2], 61, 247).

(For the estimation of the purity of thymol, *see* Seidell (Amer. Chem. J. 1912, 47, 508) ; Elion (J. Amer. Chem. Soc 1917, 39, 1513) ; Redman, Weith and Brock (J. Ind. Eng. Chem. 1913, 5, 831).)

Thymol is extensively used in medicine on account of its strong antiseptic properties. In its general behaviour it resembles carbolic acid. It has also been used internally as a vermicide. Of its derivatives a great number have been tried in medicine, but only three have been used to any extent : *Thymol iodide* (Messinger and Vortmann, Ber. 1890, 23, 2754 ; Carswell, Chem. News 1893, 68, 181 ; D.R.P. 57129, 1889) obtained by condensation of two molecules and the introduction of two atoms of iodine is used as a substitute for iodoform ; *thymoform* $[C_{10}H_{13}O]_2CH_2$ (D. R. P. 99610, 1898) used as an antiseptic dusting powder ; *thymol carbonate* $(C_{10}H_{13}O)_2CO$ (Richter, J. pr. Chem. 1883, [2] 27, 505) is used as an anthelminthic.

Camphors isomeric or homologous with thyme camphor. *Carvone*, formerly *carvol* $C_{10}H_{14}O$, b.p. 230°, is a liquid isomeride contained in the following volatile oils : Caraway seed, *Carum carvi* (Linn.) (Wallach, Annalen, 1893, 277, 107), and Dill-fruit *Anethum graveolens* (Linn.) (Gladstone, Chem. Soc. Trans. 1872, 25, 1), both

containing 50 to 60 p.c. d-*carvone*, whilst 1-*carvone* is contained in the volatile oils of Spearmint, *Mentha viridis* (Linn.) (Gladstone, *ibid.* Flückiger, Ber. 1876, 9, 473); Kuromoji, *Lindera sericea* (Bl.) (Kwasnik, Arch. Pharm. 1892, 230, 265). *i-Carvone* has been found in Ginger-grass oil, *Cymbopogon Martini* (Stapf.) (var.) *Sofia* (Walbaum and Hüthig, Schimmels, Rep. 1905, i. 34). For the isolation of carvone, its power of combining with sulphuretted hydrogen to form a crystalline hydrosulphide $(C_{10}H_{14}O)_2H_2S$, m.p. $210°–211°$, is employed (Flückiger, Ber, 1875, 9, 468; Wallach, Annalen, 1899, 305, 224); but a simpler process is to form the water soluble compound with neutral sodium bisulphite (*cf.* Sadtler, J. Soc. Chem Ind. 1904, 23, 303). On reduction carvone yields *dihydrocarveol* $C_{10}H_{18}O$, a constituent of Caraway Oil (Schimmels, Rep. 1905, i. 50).

Carvacrol, *cymophenol* $C_{10}H_{14}O$, *Iso*propyl *o*-cresol is a thick oil, solidifying at $0°$, b.p $236°–237°$, closely related to thymol. It is formed by distilling carvone in presence of sulphuric acid, phosphoric acid, or caustic potash, and occurs mainly in various thyme, origanum and monarda oils. It may also be obtained by chemical means from Spruce Turpentine (U S Pat. 1265800, 1918; *cf.* also J. Ind. Eng. Chem. 1918, 10, 982). For its identification the *phenylcarbamate* $C_{10}H_{13}OCO\cdot NHPh$, m.p. $140°$ (Gildemeister, Arch. Pharm. 1895, 233, 188) and its *nitroso-derivative* $C_{10}H_{13}O(NO)$, m.p. $153°$ (Klages, Ber. 1899, 32, 1518), are especially suitable.

Irone $C_{13}H_{20}O$ is a constituent of oil of orris, the product of distillation of *Iris germanica* (Linn.), *I. pallida* (Lam.), and *I. florentina* (Linn.) (Tiemann and Kruger, Ber 1893, 26, 2675) In the diluted state it has an odour of violets. B.p. $111°–112°$ at 2 mm., $144°$ at 16 mm. It has been synthesized from acetone and Δ_4-cyclocitral (Merling and Welde, Annalen, 1909, 366, 119), *see* PERFUMES.

Santalol $C_{15}H_{24}O$ is a liquid camphor obtained from the volatile oil of sandalwood, *Santalum album* (Linn.). The commercial product known under various trade names is prepared by steam distillation of the finely divided sandalwood. The bulk of the world's supply comes from Mysore, where it was being distilled locally (Perf. and Essent. Oil Rec. 1917, 8, 359). The physiological action of the oil is attributed to its alcoholic constituent, santalol, which is present to the extent of about 90 p.c., and has been separated into *α-santalol*, a thick colourless liquid with a faint odour of sandalwood, b.p. $301°–302°$, $[\alpha]_D + 1° 13'$, and *β-santalol*, b.p. $158°$ at 5 mm., $[\alpha]_D - 41°47'$ (von Soden, Arch. Pharm. 1900, 238, 353, Schimmels, Rep. 1910, ii. 107).

The oxygen content of the foregoing camphors is one atom. The following contain two atoms of oxygen: *Diosphenol*, *Buchu camphor* $C_{10}H_{16}O_2$, a crystalline separation from oil of Buchu leaves, *Barosma betulina* (Bartl.), *B. crenulata* (Hook.), B. *serratifolia* (Willd.) (Flückiger, Pharm. J. 1880, [3] 11, 174, 219), is closely related to thymol and carvacrol, into which it passes quantitatively by the action of concentrated hydrochloric acid at $150°–180°$. M.p. $83°–84°$, b.p. $109°–110°$ at 10 mm. It is

characterised by its reduction of ammoniacal silver solution and Fehling's solution (Semmler and McKenzie, Ber. 1906, 39, 1158; Kondakoff and Bachtscheef, J. pr. Chem. 1901, [2] 63, 61).

Inula or *Alant camphor*, *alantolactone* $C_{15}H_{20}O_2$ is the chief constituent of oil of Elecampane, *Inula Helenium* (Linn.) (Kallen, Dissert. Rostock, 1895). M.p. $76°$, b.p. $275°$, with partial decomposition (Bredt. and Posth, Annalen, 1895, 285, 349). It dissolves in alkalis with formation of the corresponding *hydroxy acid*, which melts at $94°$. The lactone has been used in medicine, under the name 'helenin,' as an antiseptic for internal use. (*See* also Sprinz, Arch. Pharm. 1901, 239, 201.)

H. R.

CAMPHORAL. Trade name for the camphoric acid ester of santalol.

CAMPHOSAN. A solution of camphoric acid methyl ester in santalol.

CAMWOOD. Camwood or 'cambe wood,' stated to be derived from a variety of *Baphia nitida* (*cf* barwood), is very similar in general properties to the other 'insoluble red' dyewoods It is, however, more expensive, yields deeper shades on dyeing, and its colouring matter is said to be more soluble than that present in the other woods

It has been examined by O'Neill and Perkin (Chem. Soc. Trans. 1918, 113, 126), who employed for this purpose similar methods to those found serviceable with sanderswood (*l.c.*).

Iso-santalin, the main colouring matter, forms a chocolate-coloured powder, which on grinding becomes redder in appearance, and is readily soluble in boiling methylated spirit. When heated, it shows no sign of melting, darkens at $280°$, and is fully decomposed at $290°–390°$, being then a carbonaceous powder. It possesses the formula $C_{27}H_{16}O_6(OCH_3)_2$, gives with alcoholic potassium acetate the salt $C_{96}H_{53}O_{32}K$ or $C_{72}H_{45}O_{24}K$, shows evidence of the formation of soluble oxonium salts, and in general properties closely resembles its isomer santalin. The colour reactions and also the dyeing properties of the two compounds indicate, however, that they are distinct substances :—

	Santalin.	Iso-santalin
Alcoholic hydrobromic acid .	Crimson.	Reddish-violet.
Dilute sodium hydroxide . .	Dull red.	Dull violet.
Alcoholic ferric chloride . .	Violet.	Bluish-violet.

For dyeing the colouring matter in alcoholic solution was added to the water in the dye-bath and the dyeings were carried out (*a*) employing wool alone, (*b*) employing wool alone and subsequently saddening with bichrome, (*c*) employing wool mordanted with bichrome and cream of tartar, and (*d*) employing wool mordanted with bichrome and sulphuric acid.

	(*a*)	(*b*)
Santalin . .	Pale dull red.	Dull reddish-brown.

	(*c*)	(*d*)
Santalin . .	Pale reddish-pink.	Pale red-pink.

Iso-santalin . Pale violet- (a) Dull violet- (b)
red. maroon.

Iso-santalin . Violet-red. (c) Violet-red (d)
weaker than (c).

Acetyl iso-santalin $C_{24}H_{18}O_8(C_2H_3O)_4$, consists of a deep salmon-coloured powder, and does not possess a definite melting-point, being gradually decomposed without fusion between 250°–280°. A molecular weight determination employing naphthalene gave the high figure 2344, a result very similar to that given in these circumstances by acetyl-santalin itself, and which may possibly be due to the production of a colloidal solution.

Deoxy-iso-santalin $C_{24}H_{18}O_2(OCH_3)_2$, corresponding to the deoxysantalin of sanderswood, is a scarlet amorphous powder which has not yet been obtained in a definitely crystalline condition. When heated, it did not show a distinct melting-point, but decomposed at 160°–165° with evolution of gas. A solution of this substance in absolute alcohol gives no immediate precipitate with potassium acetate, as happens in the case of iso-santalin, and only when excess of the reagent is employed is a gelatinous deposit formed.

A comparison of the colour reactions and dyeing properties of deoxy-iso-santalin (a) and deoxy-santalin (b) is given in the following table :—

	(a)	(b)
Alcoholic solution	Orange	Orange-brown.
Alcoholic hydrobromic acid	Bright crimson.	Scarlet.
Dilute sodium hydroxide	Crimson-scarlet.	Scarlet
Alcoholic ferric chloride	Violet.	Maroon.

The dyeing experiments were carried out by the same methods as those described above.

	(a)	(b)
Deoxy-iso-santalin	Pale red-violet.	Red puce.
	(c)	(d)
Deoxy-iso-santalin	Dull red-violet.	Pale dull red-violet.
	(a)	(b)
Deoxy-santalin	Red.	Dull bluish-red.
	(c)	(d)
Deoxy-santalin	Dull crimson	Red.

Acetyl-deoxy-iso-santalin $C_{24}H_{20}O_7(C_2H_3O)_4$, when heated, fused and decomposed at 170°–175°. It consists of an almost colourless powder differing considerably in appearance from acetyl-iso-santalin. A molecular weight determination, employing naphthalene as solvent, gave the figure 1324, which is approximately half that found in the same circumstances for acetyl-iso-santalin.

By exhaustion with alcohol the sample of camwood employed by these authors gave 16 p.c. of extract.

Camwood does not appear to contain either ptero-carpin or homoptero-carpin. A. G. P.

CANADA BALSAM *v.* BALSAMS ; and OLEO-RESINS.

CANADA PITCH or **HEMLOCK SPRUCE RESIN** *v.* RESINS.

CANADINE. A member of the isoquinoline group of alkaloids, occurring together with hydrastine and berberine in *Hydrastis Canadensis. See* under HYDRASTINE.

CANADIUM. A term formerly applied to a supposed new element ; now used to denote an alloy of 1 part palladium, 2 parts of platinum, and 6 parts of nickel, used as a substitute for platinum. It has similar resisting powers, and melts at about 1570°. Its cost is about half that of platinum (Heath, Met. and Chem. Eng. 1917, 17, 666).

CANADOL. Petroleum ether or ligroin. That portion of refined petroleum which boils at about 60° and has sp.gr. of 0·65 to 0·70 ; consists mainly of normal hexane (*v.* PARAFFIN ; and PETROLEUM).

CANANGA OIL *v.* OILS, ESSENTIAL.

CANARIN. A yellow colouring matter obtained by the action of bromine or a mixture of potassium chlorate and hydrochloric acid or ammonium persulphate upon potassium or ammonium thiocyanate ; it probably consists of $C_8H_6ON_8S_7$ (Goldberg, J. pr Chem. 1901, ii, 63, 465 ; 64, 439 ; *cf.* H. Schmid, Dingl. poly. J. 251, 41) (For details of mode of preparation, *v. ibid* 253, 130 ; also J. Soc. Chem. Ind. 3, 476). Cloth dyed with canarin resists light and soap. Neither concentrated acids nor alkalis destroy it or dissolve it out of the fibre. Bleaching powder has no action upon it. Acts as a mordant for basic aniline dyes.

CANDELILLA WAX. Candelilla wax occurs as a deposit on the surface of the candelilla plant (probably *Euphorbia antisyphilitica*), which grows wild in Mexico and Texas. Originally the wax was separated by boiling the parts of the plant with water, but of recent years a method of extraction with chloroform has been introduced, some of the works being capable of dealing with 5 tons a day. From 2·5 to 6 p.c. of crude wax is obtained, and is purified by straining and melting in water containing 0·5 to 1 p.c. of sulphuric acid. The crude grey product contains up to 6·5 p.c. of water, 3 to 15 p.c. of dirt and 0·5 to 1·5 p.c. of mineral matter. The purer red or brown variety is probably obtained by the extraction method (Berg, Chem. Zeit. 1914, 38, 1162).

Several methods of extraction have been patented. In Sharp's process (U.S. Pat. 1018589, 1912) the wax plant is boiled with petroleum spirit in the presence of fuller's earth, the extract clarified, and the solvent evaporated. In Watson's patent the plants are heated to 149°, and subjected to the action of a downward current of steam (U.S. Pats. 1042992, 1912, and 1058648, 1913). A special form of extractor devised by Thatcher (U.S. Pat. 1056378, 1913) comprises a digesting compartment, reservoir for the solvent, and vaporisers to evaporate the solvent.

The crude greenish-grey wax melts at 67°–68°, and has sp.gr. at 15°, 0·9825–0·9850 ; acid value 12·4–14·39 ; saponification value,

46·1–64·9 ; iodine value, 16·6–36·8 ; un-
saponifiable matter, 77–91·2 p.c., largely con-
sisting of hydrocarbons. The constituents
identified include hentriacontane, dotriocontane
(m.p. 71°), myricyl alcohol, two cholesterols, an
oxylactone (m.p. 88°), and resinous constituents
giving the Liebermann-Storch reaction (Fraps
and Rather, J. Ind. Eng. Chem. 1910, 2, 454 ;
Hare and Bjerregaard, *ibid.* 1910, 2, 203 ;
Sanders, Chem. Soc. Proc. 1911, 250 ; Meyer and
Soyka, Monatsh. Chem, 1913, 34, 1159 ; Berg. *l.c.*).

A difficulty attending the use of the pure
brown or red wax, is that it can only be bleached
after the addition of a considerable quantity of
paraffin wax, and is therefore only suitable for
the manufacture of inferior kinds of varnish,
for insulating telephone wires, and especially
for boot polishes, for which its low m.p. is an
advantage. For other purposes, such as candle-
making, it is inferior to carnauba wax (m.p.
83 91°) (*v.* WAXES).   C. A. M.

CANDLES. Candles represent some of the
most ancient and most useful forms of illumi-
nants. The excellence of a candle depends on
the nature of the wick and of the combustible
matter, and on the manner and extent in which
these are apportioned. The prototype of the
candle was undoubtedly the torch, which must
be regarded as a huge wick with the minimum
amount of combustible matter, this proportion
being gradually altered until the ratio used at
present, viz. about 1 part wick to 50 parts of
combustible matter, is reached.

*The following table shows the stages in the develop-
ment of candles.*

Torch. Pine branches or slips (Lat. *tœda*),
saturated, naturally or artificially, with
resinous or fatty matter.

Link. Rope-strands steeped in rosin, tar, or
pitch ; in olden times, doubtless, in
asphalt or bitumen.

Flambeau. A core of hemp, soaked in rosin
and coated with crude beeswax. Later,
the outer coat was made of bleached wax.

Dips. Wicks of rush-pith (rush-lights), crude
flax or cotton, and subsequently of twisted
cotton yarn, coated with beeswax or tallow
by repeated dippings.

Moulds. (Introduced about the 15th century
by the Sieur de Brez.) Hard tallow, sper-
maceti, stearine, or paraffin wax, cast
round the wick in a mould.

In addition to these varieties may be men-
tioned *rolled, poured,* and *drawn* candles.

Dips, the cheapest, as well as the oldest form
of candle, were made until comparatively lately
of tallow or household grease. Beeswax candles
were usually poured, drawn, or rolled. The
great advantage of the ' dip ' lies in the ease
with which it can be made. The thrifty house-
keeper was wont to set aside the superfluous
kitchen fat for melting day, when part went to
make soap, whilst the harder portions were
formed into candles. The fat was thrown into
boiling water and boiled three or four times with
a little salt to ' render ' it. The dirt and im-
purities being removed by subsidence, the clean
liquid fat was run through a strainer into the
candle pan. Some skill and experience were
required to regulate the temperature of the
melted fat. If too hot, the liquid fat would run

off the wicks ; if too cold, the material would
congeal too quickly and adhere to the wicks
irregularly and in lumps. In households these
would be rushes, divested of their peel with the
exception of a thin strip which was left to give
strength to the pith. These were usually tied
in bunches of four, so that one wick could be
held between each pair of fingers, and thus be
immersed in the liquid fat. A short time was
allowed for each dipping to cool the last coat.
Four dippings mostly sufficed, when the finished
candles were hung up in an airy loft to harden
and whiten.

In dips as manufactured on a large scale, the
wicks are of twisted cotton, and are strung on
rods, each rod holding eight. The workman,
holding an end of the rod in either hand, first
immerses the wicks in very hot tallow, in order
that their fibres may be thoroughly saturated,
and then, as each rod is ready, it is slid on to a
cross frame to cool ; the wicks are then re-
dipped in tallow at a temperature little above
its solidifying point, till the desired weight is
obtained. As a rule four ' dippings ' are required.

Many devices exist for reducing labour and
ensuring uniformity of result in manufacturing
dips. Of these contrivances, the ' Edinburgh
wheel ' is the best known. It consists of a long
pole, pivoted vertically, and having mortises
cut about its centre through which pass long
wooden bars, each pivoted at its centre on an
iron pin. These bars carry frames at their ex-
tremities, each of which, in its turn, holds about
eight wick-rods. The post revolves, and as
each bar with its frame passes over the melting
pan, it is pulled down, so as to immerse the
wicks. The opposite frame restores equili-
brium, and the rotating and dipping are con-
tinued until the proper weight is obtained,
which is signalled by some contrivance on the
post, itself the object of much inventive in-
genuity. The most perfect apparatus of this
kind was patented by Price's Candle Company
and worked at the Inventions Exhibition in
London in 1885.

Rolled, poured, and drawn candles. Rolled
candles are now almost obsolete. Formerly, the
larger sizes of church candles were made by
' rolling ' a cake of warm wax, kneaded until it
was plastic, round a wick, and imparting the
necessary smoothness and uniformity by means
of a rolling-pin. This process has now been
entirely superseded by that of ' pouring.'
' Drawing ' is resorted to only in the case of
' cables ' of small sizes, and tapers.

In *pouring,* an apparatus similar to that used
in dipping is employed, but instead of the
wicks being dipped, the melted beeswax is
poured over them while the frame is kept in
rotation (Fig. 1). In the larger sizes, the wicks
have to be reversed from time to time to ensure
a uniform thickness. The workman ascertains
the correct dimensions by measuring with a
piece of tape. After every two or three pourings,
according to the weather, the hoops are hung in
a current of air to cool. When the candles are
of the requisite thickness, they are severed from
the frame and placed on a smooth marble slab.
The operator then rolls them to and fro under a
board, on which he leans with his full weight.
By this process, which requires much skill and
practice, the irregularities are smoothed away,

and the candles, in the hands of a skilful workman, assume the evenness of outline of moulded candles, with a peculiar softness, indescribable, though unmistakable when once identified. The ends of the candles are now cut clean with a sharp knife, and their tips shaped with the finger and a small strip of wood.
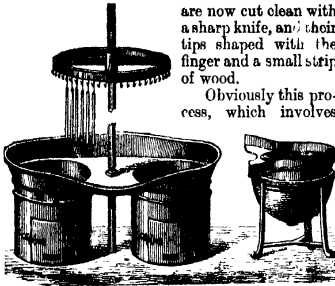
Obviously this process, which involves

FIG. 1.

much skilled labour, must render beeswax candles very expensive. They are, indeed, the most costly form of illuminant. Their use is confined to churches and, to a small extent, to carriage lamps, in which formerly no other candle could be employed, by reason of the strong spring, although now several efficient substitutes exist and are in use.

To understand the favour which beeswax continued to enjoy long after the introduction of stearine and paraffin wax candles, which are not only much cheaper, but give a better light, we must take several circumstances into account. The first and, doubtless, the most cogent fact lies in the sharp contrast which formerly obtained between beeswax and tallow, a contrast which finds mention in many a tale of social life, even as far back as the times of Haroun Alraschid. The candle at one period was absolutely the only means of illumination available, and formed a very considerable item in the household expenses. As only the rich could afford this luxury, the beeswax candle became intimately associated with the other signs of wealth, as essential, indeed, as arms or silver plate. The introduction of spermaceti, in the middle of the 18th century, greatly affected the use of beeswax, and this was quickly followed by the adoption of gas in houses. Within the last decades, the electric light has replaced both beeswax and spermaceti candles in houses where for centuries no other light was known.

To adapt the beeswax as it comes from the hive to the requirements of the chandler, but little is needed beyond the ordinary cleansing processes. The clean beeswax is run from the ' copper ' over a rapidly rotating drum into cold water, by which means it becomes divided into fine shavings. These are exposed to the influences of sun and air for several weeks, with occasional re-meltings and pourings, after which the now cream-white wax is ready for use.

Drawn candles are made by *drawing* a considerable length of wick through a bath of beeswax (Fig. 2), maintained at a regulated temperature by (fire or) steam. The wick is wound from one drum on to another. As it leaves the pan, it traverses a plate perforated with holes in

creasing from one sixteenth of an inch to half an inch in diameter, whereby the superfluous wax is stripped off, the coated wick as it emerges, being of the diameter of the hole. When the wick is all wound off, the drums are reversed, the end of the coated cotton passed through the
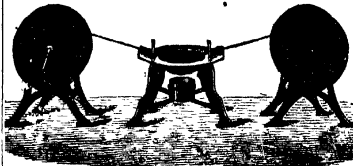

FIG. 2.

hole next in size, and the operation continued till the requisite thickness is obtained. This is seldom over half an inch, as the risk of cracking increases considerably with the diameter of the cable. In fact, this process is resorted to mainly for manufacturing ' spills ' or lighting-wicks and the little tapers used for decorating Christmastrees, but here also stearine in the former and paraffin wax in the latter have gradually displaced beeswax.

Mould Candles.—The chief variety of candles now made are mould candles. In order to ensure the proper burning of a candle, great attention must be bestowed upon the preparation of the wick, which is to the candle what the burner is to the gas. Till about 1820 the only wicks used were made of twisted cotton yarn, still to be seen in tallow dips. No means for consuming the wick being employed, snuffers had to be used to remove the charred and glowing end. Several expedients were devised to bring the wick automatically into contact with the air, and thus cause it to be consumed as the candle burnt. The best of these consisted in twisting the wick round a rod, and while in a state of tension, coating one side with size or other stiffening. This imparted a tendency to turn outwards and curl over, which to a great extent obviated the use of snuffers. Palmer, in 1852, invented a simple means for achieving the same result more thoroughly by introducing a fine thread coated with metallic bismuth into the substance of the wick, which thread he called the ' doctor.' When ignited, the easily fusible metal formed a globule on the end of the cotton, which by its weight bent the wick out of the flame into the air, when the oxygen could combine with the incandescent carbon, whilst the bismuth was volatilised. So successful was this device, that Palmer's ' metallic wick ' candles achieved great popularity, especially for burning in candle lamps, for which large candles, sometimes weighing two pounds, were employed. The same device was again patented in Germany, by Varenkamp, as late as 1899.

But the introduction of ' braided ' or ' plaited' wicks by Cambacères (in 1825) rendered such precautions unnecessary, the flat form of the wick, as now made, imparting a sufficient tendency to curve and bend outside the flame, where the cotton can burn completely. Now all except tallow dip candles are provided with these cores.

Before the wick can be used by the candle maker, it has to be ' pickled,' *i.e.* soaked in a

solution of certain chemicals, which vary with the nature and purpose of the cotton. The preparation of these solutions forms one of the chief items in the manufacture of a good candle, and to carry it out thoroughly demands considerable practical experience; for the wick itself varies much in its composition, especially as regards the percentage of mineral matter. The plait, too, will vary in tightness, however carefully woven. Then again, a paraffin candle requires a thin wick to check a too-rapid supply of the liquid fuel. A beeswax or sperm candle, on the other hand, the melted material of which is less mobile, or has less tendency to smoke, needs a thicker wick. The nature of the combustible, its melting-point, viscosity, and burning powers; the compounding of a suitable material by mixing candle materials from several sources; the selection of a wick that in number of threads, structure, and substance is adapted to the special material chosen; the subsequent treatment of this with such salts as will correct or enhance its tendencies;—these are some of the points which must be considered before proceeding with the more mechanical operations involved in candle making.

The wicks, which arrive at the factory from the cotton spinner in hanks, are placed two or three days before being wanted in the appropriate pickling solution. The object of 'pickling' the wick is to counteract either 'ashing' or 'smoking,' two great defects to which the candle is liable. The 'pickling' retards the too rapid combustion of the cotton, and vitrifies it slightly, so that when the wick protrudes from the flame any ash can drop off readily. In order to ensure the ready lighting of a candle, it has been proposed (Haase, Fr. Pat. 342527) to impregnate the protruding end of the wick with a solution of celluloid in acetone. Borax, nitre, sal ammoniac, potassium chloride or chlorate, and ammonium phosphate, are the principal salts employed for pickling; though almost every manufacturer has his own recipe. The proportion of the salt to water is usually about 2 oz. to 1 quart. The wicks are steeped in the solution for about 24 hours, after which they are placed on a perforated shelf, to allow the bulk of the liquid to drain off, and then transferred to a centrifugal machine rotating at a speed of nearly 1000 revolutions a minute, where the residual water is expelled without the slightest torsion or other disturbance in the structure of the threads, which would be almost inevitable in any other process. The hanks, still slightly damp, are placed in a cupboard heated by steam, and finally hung up in an airy room until required. The amount of salt remaining in the fibre must, of course, be very small, but it is quite sufficient to influence materially the burning of the candle. The wick is next transferred to the spools, from which it passes to the moulding machine. This task is performed by boys, who wind the wick off the hank previously stretched on a circular rotating frame, on to 'spools' or bobbins on spindles (Fig. 3). As they wind, they let the wick run through their fingers, to detect any knots or other irregularities, which might interfere with the burning of the candle. The spools are now ready for transport to the machine, invented by Cahouet in 1850. The old 'hand-frame,' the forerunner and prototype of the present compli-

cated apparatus, consists of a cluster of pewter moulds, introduced in 1724 by Freitag, held together by wooden collars at either end. Each mould is traversed longitudinally by a wick, which is secured by a peg at the top and wire at the base, and it has to be provided with a
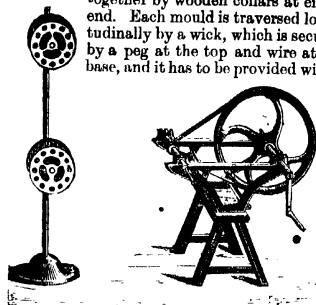

FIG. 3

little loop of cotton, through which a wire is passed. The butt ends of the moulds open into a trough about 1 inch deep. Into this the hot material is poured until it is quite filled, and the whole frame is then placed in a tank of water, the temperature of which varies with the quality of candle, as will be explained presently. When quite cold, the candles are removed from the pipes by simply inverting the frame, the cake of superfluous candle material having been previously scraped off, and the wires and pegs withdrawn. As the pipes are made slightly conical and as the substance shrinks in cooling, there is seldom any difficulty in emptying the frame; if one or two of the candles should refuse to leave the moulds, a slight tap with a mallet speedily loosens them. This method is obviously slow and cumbrous, and were it not that some buyers will have hand-made goods, also that a few odd sizes for which it would not be worth while to keep special machines can only be made in hand-frames, these frames would have been abandoned long since. A hand-frame can be filled and emptied once an hour, whilst a modern machine will do thrice the amount of work in the same time.

Fig. 4 represents a candle machine of modern manufacture, for making candles with ordinary, i.e. not self-fitting, ends. It embodies the combined inventions and improvements made successively by Sampson (Eng. Pat. 2108, 1796); Binns (Eng. Pat. 2488, 1801); Morgan (Eng. Pat. 6610, 1834); Tuck (Eng. Pat. 7409, 1837); Palmer (Eng. Pat. 12077, 1848); Cowper (Eng. Pat. 1988, 1856); Humiston (Eng. Pat., in the name of Newton, 2541, 1857); Stainthorp (Eng. Pat., in the name of Pitman, 2556, 1857); Stainthorp (Eng. Pat. 740, 1860). The machine consists mainly of a metal tank, G, in which the pipes are fixed with their butts opening in a trough and their tips emerging below. The tips are not of one piece with the moulds, but can slide up and down, fitting water-tight when drawn home. The motion is communicated by pistons, D, to which the tips are soldered, and which are perforated longitudinally.

The wicks wound on the above-mentioned spools, which rotate on a series of spindles at

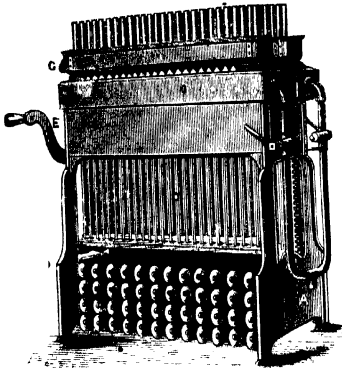the base of the machine, pass up these perforations D. The tank G, which surrounds the

FIG. 4.

pipes, is preferably connected with hot and cold water cisterns, or with cold water and steam The moulds are made of pewter (an alloy of tin and lead), other materials, such as tin, brass, glass, &c., not having been found suitable in practice. Porcelain moulds have been patented for paraffin candles (Ger. Pat. 195702), but it is very unlikely that they will be adopted in candle works, as they are too costly; moreover properly cleaned pewter moulds impart the same lustre to a candle that the porcelain mould gives. To begin the operation of casting, the wicks are drawn through the pistons, tips, and pipes, and temporarily secured in the troughs. These, and the moulds opening into them, are now filled roughly, merely to afford a starting-point for the wick, and emptied as soon as the material is cold. To effect this, the trough is scraped clear with a 'spud' (a blunt knife of the width of the trough), after which the handle E is slowly turned. This imparts, by means of rack-and-pinion gear, a vertical motion to the pistons, which mount up the pipes, carrying the dummy candles with them, and unwinding the wick from the spools. As the candles emerge from the pipes, they are received in a clamp frame C, which is held open by a spring handle. When the tips are clear of the trough, the clamp is closed, gripping the candles firmly. The handle is now turned the reverse way, causing the pistons to descend in the moulds till the tips close the ends securely. Thus the wicks
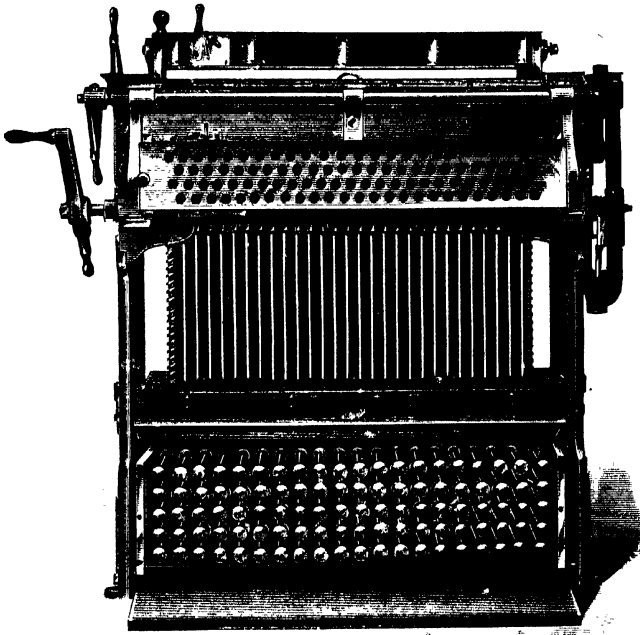

FIG. 5.—Multiple moulding machine.

are left in the centre of the pipes, held by the dummies above and the spools below. The most recent type of this machine is shown in Fig. 5. The next step depends on the nature of

the material used. If stearine candles are to be made, the tanks are charged with tepid water, the temperature of which the operator determines by his hand in preference to other methods. The reason for this precaution depends upon the highly crystalline structure of ' stearic ' acid (' stearine '), which renders it liable to crack if chilled too suddenly, or to crystallise if cooled too slowly, whereby the appearance if not the structure of the candle would be impaired Therefore the melted stearine is stirred, with the aid of simple machinery, in the melting pans, till it assumes the consistency and appearance of gruel, in which state it is transferred to the ' jacks,' cans having a flat, wide spout, and thence to the moulds. When these are full, they are allowed to rest about 25 minutes until they are sufficiently hard to permit of their being withdrawn without fracture. The troughs are not scraped in this case, as the tops are hard enough if the candles are raised 2 inches. As soon as the pipes are filled again and the material set sufficiently to hold the wick without extraneous acid, the upper row of candles, often while still warm, is removed into trays where they cool and bleach. This tendency of stearine to crack was a great obstacle to the success of these candles when they were first introduced. Among the various devices employed to overcome the defect was that of stirring a small proportion of arsenic into the melted stearine. This certainly broke the grain, but it was of course diffused into the air on burning the candles. When this became generally known, the prejudice against stearine candles was such as to affect injuriously the success of the new substitute for tallow, and to this day stearine candles enjoy but a comparatively limited popularity in this country.

In a patent process for preparing the fatty acids for stearine candles (Reuter Process Co., Eng. Pats. 9393 and 9394, 1915), the glycerides are fractionally saponified by boiling with sulphonic acids, such as Twitchell's reagent (Eng. Pat. 4741, 1908). It is claimed that candles made from the resulting fatty acids are not decolourised by an exposure of several days to the sun and air.

Paraffin Candles.— At present, stearine candles are replaced in this country by candles made of a mixture of stearine and paraffin wax, except in the case of hollow candles (*see* below). In France, however, the stearine candle, being protected by customs duties on paraffin wax, holds its own against paraffin candles; and in that country, as also in Italy, stearine candles are manufactured in considerable quantities In Germany and Austro-Hungary. the stearine candle is gradually being ousted by the paraffin candle When, in 1854, James Young obtained from shale oil a pure white paraffin, which was subsequently made into candles under a patent of J. K. Field, the immediate popularity of the novel illuminant left little doubt as to what would be the material of the candle of the future. Even the most enthusiastic optimist of that day would have hesitated before accepting the prophecy that paraffin candles would be sold at half the price of tallow dips, as is the case to-day.

The main difficulty experienced in the early stages of the manufacture of paraffin candles arose from want of precaution in regulating the temperature while casting. The same machine can be employed for either paraffin or stearine candles, but when paraffin wax is to be used, the water in the tanks is raised to a temperature of nearly 200° F., by passing steam through the pipe. Also the paraffin wax itself is heated to about 170°-180° F., and poured in a highly mobile state. When the pipes are filled, the hot water is discharged from the tanks and cold water immediately introduced, thus suddenly chilling the fluid material. If the exact point be missed, failure will result. Thus, if the pipes are colder than the inflowing paraffin wax, it will congeal as it touches the metal, assuming a dull, striated aspect. On the other hand, if the moulds are allowed to cool slowly, the candles will shrink on to, instead of from, the walls, and will be injured in removal from the moulds, if indeed they can be withdrawn at all in the solid state. When the operation is properly carried out, and the pipes are not worn by usage, and further, if the paraffin is highly refined and of a high melting-point, the candles leave the moulds with a lustre which hardly suffers by ordinary handling. This lustre, combined with the translucency, snowy whiteness, and ready adaptability to ornament in shape and colour, gives paraffin wax the pre-eminence over all other materials for candle making. It has, however, its disadvantages. The readiness with which it liquefies by heat, gives to even the best paraffin candles a tendency to 'gutter.' Moreover, the paraffin wax has the peculiar property, which is independent of the melting-point, of becoming plastic after exposure to a moderate degree of heat. The time required to develop this tendency varies, it is true, with the hardness or fusibility of the paraffin wax, which ranges from 108° F. to 140° F. : but even ceresin, of a melting-point of 142°-143° F., is affected by protracted heat. The inferior varieties of paraffin candles, from the ease with which their substance melts, are very prone to smoke ; the wick is apt to be too abundantly supplied with combustible, and is consequently chilled below the point at which complete combustion can take place.

By judiciously mixing stearin and paraffin wax, the candle maker is able to obviate many of the defects of the substances, whilst retaining their advantages. Such candles as ' petro-stearine,' ' palmitine,' and other popular varieties and especially the paraffin candles of the Saxo-Thuringian paraffin-wax industry, are made on this principle.

In the United States the method of preparing such composite candles is to melt the paraffin wax by means of steam, to add a small proportion of stearine, and to clarify the mixture by the addition of oxalic acid, which precipitates calcium salts. The clear upper layer of wax is then drawn off into a steam-jacketed pan, where it is heated, and impurities are detected and separated, after which it is transferred by means of a ' swimmer ' to a ' jack ' or bucket, which delivers it in a regulated stream to the moulding machine (Campbell, J. Inst. Petrol. Techn. 1916, 2, 274).

In Laursen-Schjödt's process (Fr. Pat. 466027, 1913), oleine or stearine is dissolved in turpentine or other solvent, the solution treated with the calculated amount of alkali for saponification, and the resulting mass incorporated with paraffin wax.

The use of trimethylamine in the manufacture of composite candles has been patented by Herzmann (D. R. P. 275344, 1911), the trimethylamine being treated first at the ordinary temperature, and then under pressure at 150° with chlor hydroxy fatty acids or sulphuric esters of hyd, xy fatty acids such as Turkey oil. The resulting product can be saponified

In Burke's patent (Eng. Pat. 14975, 1914) about 0·25 p.c. of a heavy metal salt of an organic acid (e.g. lead oleate or palmitate) is added to the paraffin wax.

The transparency of stearine and paraffin candles may be reduced by adding from 1 to 6 p.c. of 'denatured' ethyl or methyl alcohol, the amount depending upon the degree of opacity desired (Moretti, Fr. Pat. 431490, 1911).

One of the greatest improvements in candle making is the self-fitting end, by which a simple device a candle will fit any normally constructed sconce without being scraped or using paper or any other expedient to enlarge or diminish the butt. The self-fitting end patented by J. L. Field (Eng. Pat. 3032, 1861), is now in universal use.

Fig. 6 gives an example of the conical butt, whilst Fig. 7 represents the machine patented by E. Cowles for its manufactur. The difficulty to be overcome lies in the butt projecting beyond the stem of the candle, which renders the ordinary method of withdrawal impracticable. To meet this, the butts are cast
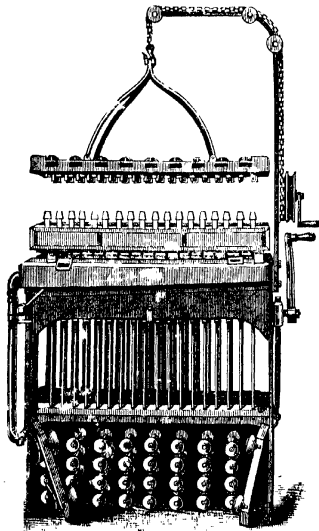
FIG. 6.

FIG. 7.

in a separate frame, which can be fitted to or removed from the pipes at will. When the machine is to be filled, the butt frame is lowered by the chain till the butts rest upon

and fit tightly into their respective pipes. The wicks are then drawn through the butt moulds with a wire and clamped in a centric position, after which the filling is proceeded with in the usual manner. When cold the wicks are cast loose, the tops scraped off, and the upper frame hoisted off the butts, as shown in the illustration, the operation being concluded as before. It will be noticed that this apparatus precludes running a continuous wick, as is done in the making of candles having plain ends; and in a large factory, a serious loss is incurred in the course of the year by the inch or two of wick snipped off at each operation. A very ingenious machine for saving this waste is due to E. Cowles, who invented a split bed-plate holding the butts. When ready for withdrawal, the butt
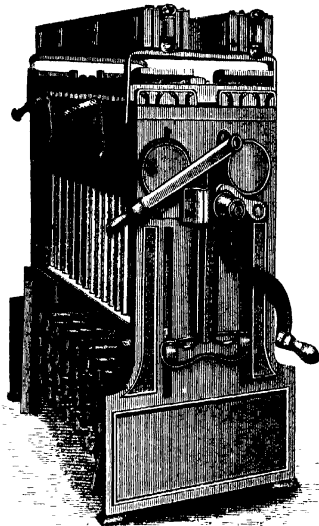

FIG. 8.

moulds are raised and opened out by a simple lever motion, and the candles can thus be passed through without further trouble (Figs. 8 and 9).

Numerous improvements have been made in the construction of candle machines by the makers in this country, in France, the United States, and Germany, but all these improvements refer to mechanical details only, without affecting the principle. All these machines work discontinuously. A continuous candle machine, for a description of which the reader must be referred to Engineering, 1901, Feb. 1st, has been constructed by Fournier et Cie, Marseille. The machine is very complicated, and would seem only to commend itself to works where a very large output can be relied upon, and where, at the same time, the works suffer from a shortage of cooling water.

An improvement, which has found more favour on the Continent than in this country, consists in perforating the stem of the candle

longitudinally so as to afford an internal escape for any combustible which would otherwise have
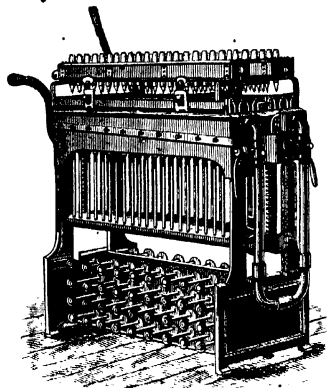

FIG 9.

guttered down the outside. The up-draught of air which takes place in the tubes has a tendency to ensure more perfect combustion. By reason of the hardness required in their manufacture, these candles must be made with stearine.

A more recent process to prevent guttering is that devised by Powell and Bush (Eng. Pat. 110579, 1916), according to which the candles are varnished with a colour varnish or with paraffin wax stiffened with a combustible powder such as cellulose.

Candles made for ordinary purposes are ready for packing immediately after leaving the candle machine Better-class candles are subjected to polishing and finishing processes in special machines, which are much more used on the Continent than in this country.

Much art has been expended on the ornamentation of candles. Before the introduction of aniline dyes, candles were coloured with such pigments as vermilion, ultramarine, and verdigris; these, besides causing a dull, heavy appearance, ruined the wick by choking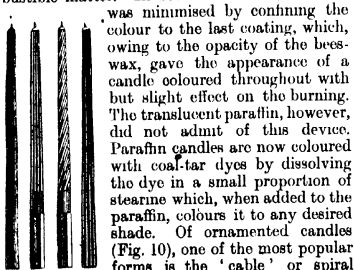 it with incombustible matter. In beeswax candles, this evil was minimised by confining the colour to the last coating, which, owing to the opacity of the beeswax, gave the appearance of a candle coloured throughout with but slight effect on the burning. The translucent paraffin, however, did not admit of this device. Paraffin candles are now coloured with coal-tar dyes by dissolving the dye in a small proportion of stearine which, when added to the paraffin, colours it to any desired shade. Of ornamented candles (Fig. 10), one of the most popular forms is the 'cable' or spiral pattern. This form, as patented by Field, was made by turning the plain candle in a lathe of complicated structure, which could fashion over thirty different sizes and patterns of candles, e.g. cabled, spiral,

FIG. 10.

fluted, striped, &c. By grooving out continuous patterns, replacing the candle in its mould, and running in coloured stearin, a number of fanciful devices were obtained, each of which had its period of popularity. The 'King Alfred's candle,' the stem of which is divided by grooves of this kind into sections burning an hour each, still enjoys favour.

The demand for cabled candles is now so large that they are made in moulds, the pistons while ascending being caused to rotate, so as to screw the candles out of their spiral moulds.

Candles burning with coloured flames have been patented by Scheurer (D. R. P. 216338, 1907), the candle material being impregnated with nitrates or other salts readily decomposing when heated, and metallic salts or wires capable of imparting a colour to the flame.

Night lights are short thick cylinders of a fat or wax, furnished with small wicks, their object being to give a constant and lasting rather than a bright light. They are usually cast direct in paper cases, and are recommended to be placed on water. Price's Candle Co. have adopted the plan of casting the cylinders in a machine similar to a candle frame, and employing a material so hard (pressed coco-nut stearine) as to retain its form in hot weather without external support. These lights are burnt in glass cups, thus shedding their full light and rendering the precaution of water unnecessary. Another very popular form of this illuminant is Clark's 'pyramid' night light, which, as its name indicates, is conform. In this, the material employed is pressed tallow of great purity, and the wick is a rush-pith with two lateral strips of the peel left adhering. These turn outwards in burning, giving a neat and shapely flame. The base of the cone is a disc of plaster of Paris, which holds the wick upright till the whole of the fat is consumed; a result achieved less surely in the other kinds, where the wick is of 'inkle' (flax), held by a little strip of tin, into which the base of the fibre is fixed.

Candles intended for heating purposes, and so burning with a hot smokeless flame, and giving only a feeble light, are prepared from esters of amino or imino acids melting between 50° and 130°, and decomposing between 200° and 300°. Ammonium nitrate or similar substance is also added (Scheuble, D. R. P. 234340, 1909).

The use of viscose filaments as a material for candle wicks has been patented by Wilson (Eng. Pat. 5170, 1913).

The strides made in gas and electric illumination have not materially affected the prosperity of candle manufacture. On the contrary, every year sees a considerable increase in the number of candles made. This is especially due to the increasing consumption of candles in mines (Transvaal, India, Australia, &c.). An inquiry made by the writer, in 1903, as to the consumption of candle material in this country, led to an estimated quantity of 45,600 tons, which may be distributed over the different materials mentioned above, as follows : tallow (for dips), 1000 tons; stearine, 2190 tons; paraffin wax, 42,200 tons; ceresin, 100 tons. France produces about 30,000 tons of candles, chiefly stearine candles; Germany, about 11,000 tons, chiefly paraffin candles; Holland, about 6000 tons, chiefly stearine candles; Belgium, about 4000 tons, chiefly stearine candles. Austro-Hungary,

Italy, and Russia produce much smaller quantities than the last-named countries.

Candles were exported from Germany to the value of £56,600 in 1912, principally to Russia, Mexico, Brazil and the Mediterranean countries. In 1912 the exports from Austria-Hungary, chiefly to the Balkan States, Russia, Turkey, and Egypt, were valued at £14,000; whilst the total exports from the United Kingdom (1913) were of the value of £435,000 (Board of Trade, Bull. No. 89).   J. L.

CANDLE-NUT OIL is obtained from the fruits of the candleberry tree, *Aleurites moluccana* (Willd.), belonging to the family of spurgeworts (*Euphorbiaceæ*). The tree attains the height of 30 or 40 feet, is a native of the Moluccas and South Pacific Islands, and is widely distributed over the tropics of the eastern hemisphere; it also occurs in the Cameroons. In India it is known as ' Indian akhrout.' The fruits resemble walnuts in their appearance, but the shell of the candle-nuts is far thicker. The name ' candle-nut ' is derived from the practice of the South Sea Islanders to dry the kernels, thread them on reeds, forming a candle, several of these candles being wrapped in a leaf of *pandanus* (screw-pine) so as to make a torch.

The average composition of the kernels is as follows :—

	Per cent.
Oil	61·0
Water	5·0
Proteins	23·0
Ash	3·4
Carbohydrates and crude fibre	7·6
	100·0

The cold-drawn oil is limpid, colourless, or yellowish; has a pleasant odour and bland taste, but cannot be used for edible purposes on account of its purging properties.

The oil extracted from a typical sample of the nuts had the following characters: sp.gr. at 15·5°, 0·9276; refractive index (25°), 1·4970; acid value, 0·8; saponification value, 188·2; and iodine value, 151·6 (Tests for Candle-nut Oil: American Soc. for Testing Materials, 1914).

The oil is obtainable in enormous quantities, but hitherto it has not been used to such an extent as its drying properties would warrant.

The fruit of *A. triloba* (Forst.) is two-celled, fleshy, olive-coloured, and about two and a half inches in diameter. Each cell contains one nut, resembling in appearance and taste a walnut, the shell of which is very hard. The seeds yield about 50 p.c. of an oil known as ' kekuna oil.' Seeds from Hong Kong, where the tree is cultivated as one of the best shade trees, were found to contain 60 p.c. of an edible oil very similar to that obtained from *A. moluccana*; whilst Mauritius seeds yielded 68·1 p.c. of oil with the following characters: sp.gr. at 15°, 0·927; saponification value, 193·7; and iodine value, 151. The nuts are worth about £28 per ton in Europe (Bull. Imp. Inst. 1912, 10, 44).   J. L.

CANELLA BARK. The dried bark of *Canella alba* (Murr.), obtained from Florida and the West Indies in large buff-coloured quills or pieces of about an inch broad. Has a bitter pungent acrid taste and odour of a mixture of cloves and cinnamon, due to a volatile oil containing *eugenic acid* which is also found in oil of cloves. The bark contains a bitter principle, *canellin*, together with resin, mannite, and starch. Used in medicine as an aromatic bitter and tonic, and in rheumatism and gout..

CANELLE or **BISMARCK BROWN** *v.* AZO-COLOURING MATTERS.

CANFIELDITE *v.* ARGYRODITE.

CANNABIN or **INDIAN HEMP RESIN** *v.* RESINS.

CANNABINENE *v.* RESINS.

CANNABINOL. The active constituent of Indian hemp resin or ' hashish ' (*v.* RESINS).
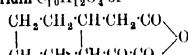
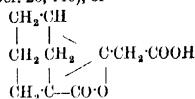**CANNABIS INDICA** *v.* RESINS.

CANNONITE *v.* EXPLOSIVES.

CANTHARIDES. *Spanish flies* (*Lytta vesicatoria*). Dried coleopterous insects used in medicine, in the form of plasters, tincture, liniments, &c., on account of their vesicating properties, due to a peculiar acrid principle, *cantharidin*.

Employed also as a stimulant diuretic, as an aphrodisiac, and as an emmenagogue. Obtained principally from Hungary, Russia, and the South of France.
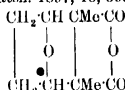
Cantharidin $C_{10}H_{12}O_4$ or

$$\begin{matrix} CH_2 \cdot CH_2 \cdot CH \cdot CH_2 \cdot CO \\ | \qquad\qquad | \qquad\quad \rangle O \\ CH_2 \cdot CH_2 \cdot CH \cdot CO \cdot CO \end{matrix}$$

(Spiegel, Ber. 26, 140), or

$$\begin{matrix} CH_2 \cdot CH \\ | \quad | \\ CH_2 \; CH_2 \quad C \cdot CH_2 \cdot COOH \\ | \qquad\quad | \\ CH_2 \cdot C\!\!-\!\!CO \cdot O \end{matrix}$$

(Meyer, Monatsh. 1897, 18, 393), or

$$\begin{matrix} CH_2 \cdot CH \; CMe \cdot CO \\ | \qquad | \qquad | \\ O \qquad\quad O \\ | \qquad \bullet| \qquad | \\ CH_2 \cdot CH \cdot CMe \cdot CO \end{matrix}$$

(Gadamer, Arch. Pharm. 1914, 252, 609 ; 1917, 255, 277 ; 1917, 255, 315) is obtained by treating the powdered insects with chloroform, ether, or ethyl acetate, acidified with sulphuric acid, evaporating the extract and treating the residue with carbon disulphide or light petroleum, to remove fat; or by mixing the cantharides with water and magnesia ; drying, treating with dilute sulphuric acid, and extracting with ether. The yield varies from 0·3 to 1·03 p.c. of the insects taken.. Crystallises in trimetric plates, melts at 218°, but begins to sublime at 85°. It is tasteless and inodorous ; blisters the skin strongly, especially when in solution or mixed with fat. Yields the alkaline salts of cantharic acid $C_{10}H_{11}O_5$, by heating with aqueous solution of potash or soda. For other derivatives of cantharidin, *see* Rudolph, Arch. Pharm. 1916, 254, 423. Gadamer has shown that the *iso*cantharidin and *iso*cantharidic acid of Anderlini and Ghira are in reality acetyl hydrato cantharic anhydride and acetyl hydrato cantharic acid respectively.

CANTON'S PHOSPHORUS *v.* CALCIUM.

CAOUTCHOUC *v.* RUBBER ; also TERPENES.

CAOUTCHOUC OIL. An oil which has proved efficient in preventing rust. It is spread with a piece of flannel in a very thin layer over the metallic surface which is to be preserved, and allowed to dry. To remove it, the article has simply to be treated with caoutchouc oil

again, and washed after 12 to 24 hours (J. Soc. Chem. Ind. 1, 315).

CAP COMPOSITIONS v. EXPLOSIVES.

CAPE BERRY WAX v. WAXES.

CAPRIC ACID or **DECOIC ACID** v. DECATOIC ACID.

CAPROIC or **HEXOIC ACIDS** C_6H_{11}·COOH. Seven isomerides are known.

1. *n-Caproic acid* $CH_3(CH_2)_4COOH$ occurs in the fats; in cheese; and, possibly, mixed with certain of its isomerides, in cocoa-nut oil; in St. John's bread; in the fruit of *Heracleum sphondylium* and in the flowers of *Satyrium hircinum*; and in the fusel-oil from the fermented molasses of mangel wurzel Is best prepared by fractionating crude fermentation butyric acid (Lieben, Rossi, Annalen, 159, 75; 165, 118); b.p. 204·5°: sp.gr. 0·9446 at 0°.

2. *Isobutyl acetic acid*, or *γ-methylvaleric acid*

$$(CH_3)_2CHCH_2CH_2COOH$$

is present in butter; may be obtained by the action of hydriodic acid upon hydroxy*iso*-caproic acid (Mielck, Annalen, 180, 57; Fittig. Rühlmann, ibid. 226, 347), or by the distillation of *iso*butylmalonic acid (König, Annalen 15, 20; Bentley and Perkin, Chem Soc Trans 1898, 487); b.p. 200°-201°; sp gr. 0 925 at 0°.

3. *Diethylacetic acid, pseudocaproic acid,* or *a-ethylbutyric acid* $(C_2H_5)_2CH·COOH$, may be obtained by the action of sodium upon acetic ester, and treatment of the product by ethyl iodide (Frankland and Duppa, Annalen, 138, 221); by boiling diethylcarbinol cyanide with potassium cyanide (Saytzeff, ibid. 193, 349); by reduction of dichlorethyl acetic ester by sodium amalgam (Markownikow, Ber. 1873, 1175); by heating sodium ethylate and sodium acetate in a stream of carbon monoxide (Geuther and Fröhlich, Annalen, 202, 308), by heating di-ethylmalonic acid at 170°-180° (Conrad, ibid. 204, 141); by heating α-diethyl-β-hydroxy-butyric acid (Schnapp, ibid. 201, 70); by heating diethylcyanacetic acid with concentrated hydrochloric acid at 160° (Hesse, ibid. 18, 749); b p. 190° (756 5 mm.); sp.gr 0·9196 at 20°/0°.

4. *Methylpropylacetic acid* or *a-methylvaleric acid* $CH_3·CH_2·CH_2·CH(CH_3)·CO_2H$ is obtained by the oxidation of its aldehyde, and by the reduction of methylacrylic acid (Lieben and Zeisel, Monatsh. 4, 37, 63); by heating α-methyl valerolactone or *iso*saccharin with hydriodic acid and red phosphorus (Liebermann and Scheibler, Ber. 1883, 1823; Kiliani, ibid. 185, 632); by heating α-methylpropyl-β-hydroxybutyric acid (Jones, Annalen, 226, 292); and by the distillation of turpentine; b.p. 193°-194°; sp.gr. 0·9279 at 18°/0°; 1 part water dissolves 0·5693 part at 17°.

5. *Methylisopropyl acetic acid, isocaproic acid,* or *aβ-dimethylbutyric acid*

$$(CH_3)_2CH·CH(CH_3)CO_2H$$
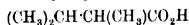
may be formed from methyl*iso*propylcarbinol cyanide (Markownikow, Zeitsch. Chem. 1860, 205); by the oxidation of the corresponding hexylalcohol from Roman camomile oil (Kobig, Annalen, 195, 102), or by melting camphoric acid with caustic alkali (Crossley and Perkin, Chem. Soc. Trans. 1898, 16); b.p. 189°-191°.

6. *Dimethylethylacetic acid* or *aa-dimethyl-propionic acid* $(CH_3)_2C(C_2H_5)CO_2H$ is formed by

the action of hydrochloric acid upon dimethylethylcarbinol cyanide (Wischnegradsky, Annalen, 174, 56), and by the oxidation of the methylethyl ketone prepared from pinacolin (Lawrinowitsch, ibid. 185, 126). A colourless liquid; b.p. 187°, m.p. −14°.

7. (a) *β-ethylbutyric acid* or *active caproic acid* $CH_3·CH(C_2H_5)CH_2COOH$ is obtained by the oxidation of the active hexylalcohol obtained from Roman camomile oil (Romburgh, Rec. trav. chim. 5, 221; Kobig, Annalen, 195. 102); b.p. 196°-198° (770 mm.); sp gr. 0·930 at 15°.

(b) *Inactive β-ethylbutyric acid* may be formed by heating secondary butylmalonic acid (Romburgh, Rec trav. chim. 6, 153) or from secondary butyliodide, diethylmalonic ester and sodium ethoxide (Kuhnsch, Monatsh. 14, 561; Bentley, Chem. Soc. Trans. 1895, 267).

CAPRYL ALCOHOL v. OCTYL ALCOHOL.

CAPRYLIC ACID v. OCTOIC ACIDS.

CAPSAICIN v. RESINS.

CAPSICUM (*Bird pepper, Cayenne pepper*). The dried ripe fruit of *Capsicum minimum* (Roxb), which was probably a native of tropical America, but is now known only in cultivation, the chief supply coming from Africa and India.

The fruit is 1-2 cm long and about one-third as broad; somewhat flattened oblong-ovoid in shape, and is covered with a crimson or scarlet, semi-transparent, wrinkled coriaceous epicarp. It is two-celled and contains about 20 yellow, flat, reniform seeds, 3 5 mm. long and 2 5 mm. broad It is prepared for use by grinding the whole fruit.

Cayenne pepper is sometimes adulterated with flour, corn-meal, or even sawdust. Entire capsicum is also frequently substituted by larger varieties. Adulteration of the powder may be detected by the estimation of oleo-resin, which should not be less than 5 p c ; and of the ash, which should not exceed 7 p c., and by micro-scopical examination (v. Bitto, Chem. Soc. Abstr 1893, D, ii 546).

The active principle of capsicum is *capsaicin* (*capsicin, capsicol*) $C_{18}H_{24}O_5N$ ($C_{18}H_{27}O_3N$, Lapworth and Royle), which is present to the extent of 0 05-0·07 p c (Morbitz, Chem. Zentr. 1897, ii. 593), ii. 593). It is obtained from the ethereal extract of capsicum, and crystallises from light petroleum in colourless plates, m p. 63 5°, easily soluble in ether, alcohol, chloroform, &c, but almost insoluble in hot water and insoluble in cold water. It is not volatile in steam, and has the properties of a weak, phenol-like acid. The benzoyl derivative forms silky needles, m.p 74° (Micko, Chem. Zentr. 1899, i. 293).

The other constituents are a volatile, non-acrid alkaloid; red colouring matter; wax; resin; fixed oil; oleic, palmitic, and stearic acids; and a minute amount of a volatile oil having the odour of parsley (Pabst. Arch. Pharm. 230, 108).

Capsicum is largely employed as a condiment. In medicine, it is used, externally as a powerful rubefacient, and internally in the treatment of atonic dyspepsia, chronic alcohol-ism, and delirium tremens.

CAPSICUM RESIN v. RESINS.

CAPTOL. Trade name for a condensation product of chloral and tannin; used in dermatology.

CAPUT MORTUUM. A term employed by

the alchemists to denote the residue remaining in the retort or alembic after the volatile matter has passed away.

CARAGHEEN MOSS. *Irish pearl moss* (*Chondrus crispus*) (*v.* CARRAGEEN ; ALGÆ).

CARAJURU, CARCURU, or **CRAJURU.** A Brazilian dyestuff of a red colour, said to be identical with *chica-red*, used by certain Indian tribes to stain their skins, and which is obtained from the leaves of the *Bignonia chica* (Humb. et Bonpland). It is a light, mealy, odourless, tasteless powder, which acquires a coppery lustre on trituration. Insoluble in water, but soluble in alcohol, ether, and alkalis (Virey, J. Pharm. 1844, 151).

CARAMEL. The brown substance produced by the action of heat on sugar glucose or invert sugar, used for colouring liquors, beer, sweet-meats and gravies.

Preparation.—On the small scale common sugar is heated, with constant stirring, in a metal pan capable of containing about ten times the quantity taken, till the whole mass melts, turns brown, and at last suddenly froths up, when the heat must be immediately stopped. Not more than 15 p.c. of the weight of the sugar should be driven off, as the product is liable to become insoluble if further heated.

For preparation of caramel colours, Asry-musry recommends the following processes (long kept secret) :—

Colour for rum.

Potassium or sodium hydroxide . 3 kilos.
Water . . . . . 6 ,,
Or potassium or sodium carbonate 4 ,,
Water . . . . . 8 ,,

Dissolve with heat in large iron pan, and add

Glucose . . . . . 120 kilos.
Or syrup of glucose . . 130 ,,

Boil over the fire till irritating vapours begin to appear, then decrease the heat and stir con-tinuously till the required shade is produced, then stop the process by adding 30 to 40 litres of water in a fine jet.

Colour for beer or vinegar.

Ammonium carbonate . . 6 kilos.
Water . . . . . 6 ,,
Glucose . . . . . 120 ,,
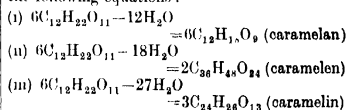
Process exactly as above.

In the modern method of manufacture the process is conducted in a closed vessel, generally with the addition of ammonia or one of its salts (*cf.* Salamon and Goldie, J. Soc. Chem. Ind. 1900, 19, 301). The colouring power of the caramel seems to depend upon the amount of ammonia used in its preparation. In McCowan's process glucose is heated with from 5 to 10 p.c. of its weight of liquor ammonia (sp.gr. 0·8803 in a closed digester to 100° for above 24 hours, and the mixture concentrated.

According to Magalhães (Compt. rend. 1896, 123, 896), caramel prepared from cane sugar differs considerably from caramel made from glucose, in that it behaves with certain reagents exactly like a coal-tar colour. Thus, when treated with basic lead acetate and then shaken with amyl alcohol, the former caramel com-municates an orange-yellow colour to the solvent, whilst with glucose caramel, no coloura-

tion occurs. Ether, when shaken with a solution of the former, acquires an orange-yellow colour, whilst with the latter no colour is extracted. Mordanted wool is dyed orange by the former, yellow by the latter. Genuine wine, to which no caramel has been added, does not give these reactions (*cf.* D'Aquiar and Da Silva, Compt. rend. 1897, 124, 408).

Properties.—Amorphous, reddish-brown, brittle mass ; porous and deliquescent ; com-pletely soluble in water, partially soluble in alcohol ; of a more or less bitter taste and non-fermentable. Melts at 134°-136°.

Little is known of the chemistry of caramel. Gélis (Ann. Chim. Phys. 1858 [iii.] 52, 352 ; 1862, [iii.] 65, 496) separated it into three amorphous substances, *caramelan*, *caramelen*, and *caramelin*, differing in solubility and colour-ing power, but not of fixed composition without definite melting-points, or crystalline derivatives and readily forming colloidal solutions. Their formation from sucrose has been represented by the following equations :—

(i) $6C_{12}H_{22}O_{11} - 12H_2O$
$= 6C_{12}H_{18}O_9$ (caramelan)

(ii) $6C_{12}H_{22}O_{11} - 18H_2O$
$= 2C_{36}H_{48}O_{24}$ (caramelen)

(iii) $6C_{12}H_{22}O_{11} - 27H_2O$
$= 3C_{24}H_{26}O_{13}$ (caramelin)

Stolle, by heating caramelan with dilute (3 p.c.) hydrochloric acid, obtained a hexose, which gave an osazone crystallising in yellow needles, melting at 179°.

Cryoscopic observations by Sabanéeff and Antushevitch (J. Russ. Chem. Soc. 25, 23) would seem to indicate that the molecular weight of caramelan is much higher than the above formula indicates. They point out that carbon dioxide, in addition to water, is given off in its formation. They allege that it is not a carbohydrate, but has the composition

$$C_{125}H_{188}O_{80}$$

and they represent its production from sugar by the equation :

$$11C_{12}H_{22}O_{11} - C_{125}H_{188}O_{80} + 7CO_2 + 27H_2O$$
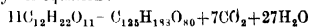
Gélis found on heating sucrose to a tempera-ture of 180°-190° that a loss of weight of 12 p.c. gave mostly caramelan, a loss of 15 p.c. Cara-melen, with a loss of 22 p.c. caramelin, was the main product. On treating the caramel with 84 p.c. alcohol the caramelan was extracted, caramelen and caramelin being insoluble in alcohol of this strength. The caramelen could be removed by cold water, when the caramelin could be dissolved out by 60 p.c. alcohol or hot water.

Caramelan, the main constituent of ordinary caramel, is a brown brittle solid of bitter taste, deliquescent and very soluble in water. Softens at 108°. The aqueous solution gives no pre-cipitate with metallic salts, but reduces silver nitrate and Barreswil's (Fehling's) solution. An alcoholic solution of lead acetate forms a precipi-tate $C_{12}H_{16}O_8,PbO$: an ammoniacal solution of lead acetate gives $C_{12}H_{16}O_9,2PbO$ (Gélis).

Caramelen is of a darker brown than car melan, and is not deliquescent. It reduces Barreswil's (Fehling's) solution and forms com-pounds with lead similar to those of caramelan. According to Gélis its composition is $C_{36}H_{48}O_{24}$

Caramelin is of a still darker brown. It appears to exist in three modifications of which A is soluble in cold water, B in boiling water, and C is insoluble. The modification A passes into B on evaporating its aqueous solution. The soluble forms reduce Barreswil's solution and give precipitates with metallic salts. All varieties have the composition $C_{96}H_{102}O_{51}$ (Géhs).

The molecular weight of 'caramel' was found by Gladstone and Tribe to be 1700, corresponding with Géhs' formula for caramelin.

Stolle (Zeitsch. Ruben-Zucker Industrie, 1899, 49, 800; 1901, 51, 836; 1903, 53, 1149) found on heating sucrose that no carbon dioxide or other volatile products were formed below 180°, and that caramelan is the sole product when this temperature is not exceeded and the loss is not greater than 12 p.c., and that its formula is $C_{12}H_{18}O_9$.

The action of heat on sucrose has been further studied by Cunningham and Dorée with special reference to the production, properties and composition of caramelan (Chem. Soc. Trans. 1917, 111, 589). They found on heating sucrose to temperature 170°-180° that, in addition to water, pungent acrid vapours, furfuraldehyde and carbon dioxide were evolved, but that if the loss of weight did not exceed 12 p.c., caramelan free from sucrose and higher caramel products was the sole product. When quite dry it melts at 136°, is readily soluble in water, 84 p.c. alcohol, pyridine, methyl alcohol, or hot glacial acetic acid, insoluble in ether and benzene. A concentrated aqueous solution acidified with hydrochloric acid gives a red precipitate with resorcinol, soluble in alcohol or alkalis. Phloroglucinol gives a similar precipitate of a deeper colour. It forms a *tetra-acetate*, yellow powder, insoluble in water or ether, but soluble in benzene, hot alcohol, or glacial acetic acid, m.p. 107°; a *tetra-benzoate*, a pale buff-coloured powder, m.p. 105°-108°, soluble in acetone, chloroform, alcohol or benzene, insoluble in water, ether, or light petroleum; a *tetranitrate*, a yellow powder which inflames violently on warming; readily soluble in ether, alcohol or benzene, insoluble in water.

It appears to be a tetra-atomic alcohol, of the molecular formula $C_{12}H_{14}O_9$, or, more probably, $C_{24}H_{36}O_{18}$. Compounds formed with phenyl-hydrazine and semicarbazide indicate the existence of one CO- or CHO-grouping per C_{24} unit. Concentrated nonoxidising acids convert it into caramelin $C_{24}H_{26}O_{13}$; weaker solutions hydrolyse and dehydrate, producing dextrose, methylfurfuraldehyde and humic acid.

Detection and estimation of caramel.

Detection of caramel in wines, &c.—10 c.c. of the liquid to be tested is mixed with 30 to 50 c.c. of paraldehyde, and enough alcohol added to make the liquids mix; if caramel is present, it forms a dirty-brown precipitate sticking to the bottom of the vessel; the solution is poured off, the precipitate washed with alcohol, dissolved in a little hot water, and the solution evaporated to 1 c.c., when different quantities of caramel may be compared by comparison of colours to confirm; this solution is mixed with one of 2 parts hydrochloride of phenylhydrazine in 20 of water, with excess of acetate of soda. Caramel yields an amorphous brown precipitate.

To detect caramel in vinegar 50 c.c. are mixed with an excess of calcium carbonate and evaporated to dryness. The mass is then extracted with 20 c.c. of ether; the ethereal solution is filtered into a test-tube containing 10 c.c. of resorcinol reagent (1 gram of resorcinol in 100 c.c. of hydrochloric acid of sp.gr. 1·125). Should caramel be present in the vinegar, a red zone is obtained at the junction of the two liquids (Ronnel, Ann. Falsif. 1912, 5, 517). The reaction is due to the presence of hydroxymethylfurfural, which also yields a violet colour with β-naphthol in sulphuric acid, and an orange-yellow colouration with phenol in sulphuric acid. The liquid to be tested, wine, vinegar, brandy, &c., is neutralised if acid, concentrated to a small bulk, extracted with ether, the ethereal extract treated with a few drops of a 5 p.c sol. of phenol in ether, and allowed to evaporate. The residue is mixed with about 5 c.c. sulphuric acid, when the characteristic colour appears (Schenk, Apoth Zeit. 1914, 29, 202; J. Soc. Chem. Ind. 1914, 369).

Amthor's method, which is the only one capable of distinguishing between caramel and the colouring matters of colour malts, is as follows· 10 c.c. of the beer or other liquid is treated with 30-50 c.c. of paraldehyde, according to the intensity of colour, and absolute alcohol is added until the liquids mix. If the mixture is left for 24 hours a brownish precipitate forms in presence of caramel. This precipitate is washed with absolute alcohol, dissolved in hot water, filtered, and the solution concentrated to 1 c.c. in vacuo over sulphuric acid. From the intensity of its colour the quantity of caramel can be estimated. Or the filtered solution of the paraldehyde precipitate may be poured in a solution of phenyl-hydrazine acetate, when if caramel be present a precipitate slowly forms, more quickly on warming. *V.* Heuss (Zeitsch. ges. Brauw. 1918, 41, 108-124; Abtr. J. Inst. Brewing, 1918, 312).

Rough test for caramel in beer.—Add a quantity of tannic acid, and shake thoroughly. If malt only is present, the colour is precipitated. Caramel colour remains unchanged. Contrary to the statement of Pasquero and Cappa the presence of furfural is not a sufficient proof of caramel unless the caramel has been added after fermentation.

Fradiss (Chem. Zentr. 1899, i. 1160) determines the amount of caramel in sugar products by treating the dry substance with methyl alcohol of 95°, evaporating on the water-bath, drying the residue *in vacuo*, or in a current of dry air, and again digesting it with methyl alcohol for 2 hours. The caramel is precipitated from the solution by amyl alcohol, the precipitate redissolved, reprecipitated once or twice more, and finally dried at 90° and weighed. The caramel may also be determined by titrating with Barreswil's solution, but if dextrose is present, it is necessary to titrate the original solution before and after treating with excess of lead acetate. Then if A=c.c. of copper solution required, *a*=c.c. of original solution required for 5 c.c. of copper solution, the volume of the copper solution, corresponding with the caramel, is 5 (*a*−A). Allowance must also be made for the amount of lead acetate solution ($\frac{1}{10}$ vol.)

used. The dextrose may also be destroyed by boiling with calcium carbonate and then precipitating with carbon dioxide. Traces of caramel are estimated by treating 200 c.c. of the solution with excess of ammoniacal lead acetate The precipitate, after washing with water free from carbonic acid, is suspended in water and decomposed with hydrogen sulphide. The filtrate is again treated with lead acetate, and the solution, from which the hydrogen sulphide has been expelled by evaporating to 10 c.c., is treated with copper solution.

Stolle (Chem. Zentr. 1899, ii. 1099) bases a method of determining caramel by means of the spectroscope on the fact that aqueous solutions of that substance partially absorb the rays of the blue end of the spectrum. The results are said to be accurate to within 0 05 p.c.

Methods for estimating the amount of caramel on the surface of coffee berries roasted with sugar, have been suggested by Neubauer, Konig, Stutzer, and Hilger. These methods have been tested by Fresenius and Grunhut (Zeitsch. anal. Chem. 1897, 36, 225), who give the preference to the method of Hilger.

Stutzer's method, which consists in shaking 10 grams of the unground coffee for 5 minutes with 250 c.c. of cold water, making up to 500 c.c., decanting, filtering, and determining the solid contents (dried at 100°), and the ash, was recommended by the Conference of Bavarian Technical Chemists. Neubauer's and Kong's processes, which depend on the extraction of the berries with hot water, give too high results.

In Hilger's process, 10 grams of whole coffee are digested three times for half an hour each time, with 100 c.c. of a mixture of equal vols. of water and 90 p.c. alcohol at ordinary temperatures. Each portion of the extract is decanted, and the united extracts are made up to 500 c.c., filtered, and residue and ash determined. If, from the numbers thus obtained, there is deducted a constant 11·07 of dry residue, or 0·83 of ash-free residue per 100 grams of dry coffee, the remainder represents the amount of caramel present.

Upsher Smith (Amer. J. Pharm. 1911, 83, 411) suggests employing the coloured solution prepared by adding Nessler's reagent to a solution of an ammonium salt as a colorimetric test. As an arbitrary value for the colour intensity of caramel, a '100 p.c.' caramel is regarded as that which has such a colouration that 10 c.c. of its 0·1 p.c. solution when treated with 2 c.c. of the Nessler reagent and diluted to 50 c.c. matches the colour obtained by mixing 10 c.c. of a solution containing 0·0417 gram of ammonium oxalate in a litre, 38 c.c. of water and 2 c.c. of Nessler solution.

CARANNA v. OLEO-RESINS.

CARAPA BARK. The bark. of *Carapa Guianensis*, has a bitter taste, and is used as a febrifuge. Said to contain an alkaloid, carapine (Petroz and Robinet, J. Pharm. 7, 293, 349).

CARAPA OIL. 'Carap Oil' or 'Crab Oil' (Fr. *Huile Carape*), is obtained from the seeds of the 'carap,' 'crappo' or 'crab-wood' tree, *Carapa Guianensis* (Aubl.), a native of the West Indies and Central America.

The oil is prepared in Trinidad for local consumption by very primitive methods. Accord-

ing to de Verteuil (Trinidad, London, 1858, 272), the seeds are gathered in June and July, boiled for 6 hours, then laid in heaps for 8 or 10 days, during which time they undergo a sort of fermentation ; they are then broken, and the pulp they contain carefully taken out and kneaded into lumps of thick paste, each about 15 lbs. This paste is laid on boards slightly incurvated and inclined, and placed in a sheltered place, when the oil oozes through the mass, and runs into a vessel placed for its reception. The paste is carefully remoulded every morning and evening, so as to favour the disengagement of the oil. After 12 days, boiling water is poured on the mass, and a fresh quantity of oil of inferior quality is thereby obtained. It is a clear yellow oil with a faint vegetable odour, and an intensely bitter taste which precludes its use as an edible oil. It is used locally as an embrocation against rheumatism and for the destruction of ticks which attack domestic animals (de Verteuil, The Agricultural Record, Trinidad, August, 1899, 17). It has considerable reputation as a liniment for dressing wounds on horses and cattle. Its excessive bitterness repels all insects, and mixed with tar is used for preserving wood. It is well suited for the manufacture of soap, and it is in this direction that its future possibilities lie.

The oil from *C. grandiflora*, from Uganda, has been examined by Lewkowitsch (Analyst, 1908, 33, 184). Good kernels contained 30·26 p.c. of oil. The colour of the cold-pressed oil was almost white, with a tinge of pale yellow. At the ordinary temperature, it solidifies. The hot-pressed oil is much darker in colour, and remains solid at the ordinary temperature.

Lewkowitsch (Analyst, 1909, 34, 10) has also examined the oil from *C. procera* (D.C.), the seeds being obtained from Sierra Leone. The sound kernels yielded by extraction with ether 57·26 p.c. of oil ; whilst the yield of oil by cold and hot extraction at a pressure of 150 atmospheres was 46·7 p.c.

The following analytical results are due to C. H. Wright (Bull. Dept. Agric. Trinidad, ix. 1910) :—

	I.	II.
Specific gravity at 40°/40°C.	0·9149	
Specific gravity at 15·5°/15·5°C.	0·9249	0·9211
Acid value . . .	27·5	19·4
Saponification value .	197·2	196·1
Iodine value . .	67·7	58·5 ·
Reichert Meissl value .	3·8	3 6
Unsaponifiable matter .	—	1·16

CARAWAY FRUIT. *Carui fructus*, B.P. The dried ripe fruit of *Carum Carvi* (Linn.).

CARAWAY OIL v. OILS, ESSENTIAL.

CARBAMIC ACID CH_3NO_2 or NH_2COOH. *Aminoformic acid.* An acid not known in the free state. *Ammonium carbamate* is, however, met with in freshly sublimed commercial ammonium carbonate, and may be prepared by mixing gaseous ammonia and carbon dioxide. Obtained also by the action of alkaline solution of potassium permanganate on albumen, leucine, tyrosine, and glycocoll.

CARBAZOLE $C_{12}H_9N$ or $\begin{array}{c} C_6H_4 \\ C_6H_4 \end{array}\!\!>\!\!NH$. A white crystalline substance found amongst the products of the distillation of coal tar, and also met with in crude anthracene. Carbazole

compounds are most easily recovered from crude anthracene by converting the former into the easily soluble nitrosocarbazole (Wirth, Eng. Pat. 14462; J. Soc. Chem. Ind. 1901, 464). May be obtained by passing vapour of aniline or diphenylamine through a red-hot tube; by boiling iminodiphenyl sulphide $HN{\displaystyle{C_6H_4 \atop C_6H_4}}S$ with reduced copper; by passing the vapour of orthoaminodiphenyl over lime heated to a dull redness (Blank, Ber. 1891, 306); or by acting on orthoaminodiphenylamine with nitrous acid and heating the phenylazimidobenzene so formed to 360° (Graebe and Ullmann Annalen, 291, 16) Forms white laminæ. m p 238°, b p. 351·5° (corr.). Carbazole dissolves in concentrated sulphuric acid to a yellow solution which changes to red-violet on heating. Addition of formaldehyde gives a blue solution changing to a greenish-blue on addition of large quantities (Gabretti, Chem. Zentr. 1907, ii. 98) 1 mol carbazole, 2 mols. salicylaldehyde and concentrated sulphuric acid, heated to 100°-110°, give an intense blue colour (Carrara, Gazz. chim. ital. 1899, n. 535).

By melting together carbazole and oxalic acid, and extracting with hot water and benzene, dissolving the residue in warm alcohol, filtering and evaporating, *carbazole blue* is obtained The alcoholic solution of carbazole blue, when treated with glacial acetic acid and zinc-dust, is decolourised. Filtered into caustic soda solution, the leuco- base separates out as a white flocculent precipitate On oxidation with any of the usual reagents, the blue colouring matter is again formed (Bamberger and Muller, Ber. 1887, 1903; J. Soc. Chem Ind 1887, 660). *Carbazole yellow* is prepared from the tetrazo- derivative of diaminocarbazole It is easily soluble in water, and dyes unmordanted cotton in a neutral bath a fast golden yellow, and wool in a neutral or acid-bath a yellow, fast to milling (Bad. Anil. and Sod. Fab. Eng. Pat. 14478 and 14479; J. Soc. Chem Ind. 1889, 771) (*v.* AZO- COLOURING MATTERS).

Nitrocarbazole is obtained by treating nitrosocarbazole with 10 times its weight of benzene and its own weight of nitric acid; sp.gr. 1·36 (Wirth, Eng. Pat. 2899; D. R. P. 128853; J. Soc. Chem. Ind. 1901, 890). Dinitrocarbazoles, *v.* Bad. Anil. u. Sod. Fab (D. R. P 46438; Frdl. ii. 447); Wirth (D. R. P. 128853; Frdl. vi. 58); Trinitrocarbazole (Akt. Ges. f. anilinfab D. R. P. 295817). These nitro- compounds may be reduced to the amino- compounds by means of alkali sulphides (Wirth, D. R. P. 139568; Chem. Zentr. 1903, i. 746). By heating carbazole with concentrated sulphuric acid, a mixture of disulphonic and trisulphonic acids is obtained. Nitration and subsequent reduction of the former yields aminocarbazole-disulphonic acid, which, when diazotised and coupled with β-naphthol, yields a dyestuff dyeing red from an acid-bath. If the nitric acid is added direct to the products of sulphonation, on reduction a second amino- acid is obtained which, when diazotised and coupled with β-naphthol, gives a red dyestuff, and with α-naphthylamine a violet (Schultz and Hauenstein, J. pr. Chem. 1907, 326). The sulphonic acids, preferably the disulphonic, condense with tetralkyldiamino diphenylcarbinol to yield

valuable green dyest iffs (Cassella & Co. Eng. Pat. 20709; J. Soc. Chem. Ind. 1909, 697). By allowing nitrosophenol, its homologues or derivatives to act on carbazole in the presence of conc. sulphuric acid, compounds are obtained which yield blue sulphide dyestuffs with alkali polysulphides (Haas, Eng. Pat. 2918; J. Soc. Chem. Ind. 1909, 517). For N-acyl derivatives of carbazole, *see* Copisarow. Chem. Soc. Trans. 1918, 816.

A method has been patented (Ch. Fab. Act. Gesell. in Hamburg, D. R. P. 81237; Ber. 1895, iv. 692) for obtaining potassium cyanide or ferrocyanide, by heating the potassium derivative of carbazole in the absence or presence of an iron salt

CARBITE. An explosive consisting of nitroglycerine (25), potassium nitrate (34), flour (38·5), barium nitrate (1), powdered bark (1), and sodium carbonate (0 5 part).

CARBODYNAMITE *v.* EXPLOSIVES.

CARBOHYDRATES. The term is applied to polyhydroxy-aldehydes and ketones, and to the substances which give these when hydrolysed by heating with mineral acids Dextrose, ordinary sugar or sucrose, starch, and cellulose are carbohydrates universally distributed in plants Dextrose and glycogen enter into the composition of animal tissues. The simple carbohydrates, monosaccharides, have the empirical composition CH_2O, the most important being those containing 5 or 6 atoms of carbon. The complex carbohydrates, polysaccharides, are built up from two or more simple carbohydrates with the elimination of water; they have the composition $(C_6H_{10}O_5)nH_2O$ (Kiliani, Chem. Zentr. 1908, 32, 366). Compounds in which n equals 4, 2, 3, or 4 are distinguished by names having the suffix -*ose*. They may be conveniently grouped as follows :—

1. Monosaccharides.
   (*a*) Pentoses $C_5H_{10}O_5$, *e g.* arabinose, xylose.
   (*b*) Hexoses $C_6H_{12}O_6$, aldoses, *e g.* dextrose, mannose, galactose; ketoses, *e g.* lævulose, sorbose.

2. Disaccharides : $n=2$. $C_{12}H_{22}O_{11}$.
   (*a*) Non-reducing, *e.g.* sucrose, trehalose.
   (*b*) Reducing, *e.g.* maltose, lactose, &c.

3. Trisaccharides : $n=3$. $C_{18}H_{32}O_{16}$. Gentianose, raffinose, melezitose.

4. Tetrasaccharides : $n=4$. $C_{24}H_{42}O_{21}$. Stachyose.

5. Polysaccharides :
   (*a*) Glycogen, inulin, dextrins, *n* unknown.
   (*b*) Starch, cellulose, *n* very large.

Related to the carbohydrates are those substances which yield simple carbohydrates, together with other substances when hydrolysed. Such are glucosides, gums, pectins, &c. (*q.v.*).

General characters.—The members of classes 1, 2, 3, 4, and 5*a* are soluble in water. They have a more or less pronounced sweet taste. The monosaccharides are colourless crystalline compounds, characterised by the power of reducing alkaline solutions of the heavy metals, for example, copper. They form characteristic compounds with phenylhydrazine.

The di- and poly-saccharides are converted into simple carbohydrates when hydrolysed. This change may be effected by means of mineral acids, or, as a rule, more quickly by enzymes. The complicated polysaccharides are usually

amorphous; they tend to form colloidal solutions, and are chemically relatively inert. In virtue of the hydroxyl- groups which they contain, they react with acetyl chloride, benzoyl chloride, nitric acid, &c., forming esters.

Carbohydrate solutions are generally optically active. The direction and amount of the rotation vary with the substance, and also with the strength of the solution, the nature of the medium, the temperature, &c. The optical rotatory power of carbohydrates is made use of in their analyses (v. Saccharimetry), and as a guide to their structure.

Interesting generalisations have been drawn by Hudson affecting the molecular rotations of α and β forms of sugars. It is now generally accepted that the difference between the molecular rotations of the α and β forms of mutarotatory sugars is a constant. The compounds selected show considerable diversity of type and discordant results have from time to time been explained away by showing that the compound in question is derived from other than the α and β forms of the sugar (cf. Hudson, J. Amer. Chem. Soc. 1917, 39, 1013). The maximum values for the specific rotations are now arrived at by the indirect method based on solubility measurements (Lowry, Chem. Soc. Trans. 1904, 85, 1551; Hudson, J. Amer. Chem. Soc. 1904, 26, 1065). The asymmetric system attached to the α-carbon atom exerts a preponderating influence on the activity of these compounds and determines the sign of the rotation.

Hudson's generalisations have enabled the optical rotatory power of carbohydrate derivatives to be used as an important guide to their structure.

Constitutional formula of Dextrose.—In addition to those carbohydrates which occur naturally, a number of others have been prepared artificially by Emil Fischer, and it is largely to his work that the present complete knowledge of the group is due. (Fischer's original work has been republished, Untersuchungen über Kohlenhydrate, Berlin, 1909, J. Springer.)

Dextrose and its isomerides $C_6H_{12}O_6$, conveniently termed glucoses, have 5 oxygen atoms present as 'hydroxyl,' since they form esters such as dextrose pentacetate

$$C_6H_7O(O \cdot CO \cdot CH_3)_5$$
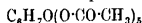
The sixth oxygen behaves as an aldehyde in dextrose and galactose, as a ketone in lævulose and sorbose. The two classes of compounds are accordingly referred to as aldoses and ketoses. Reduction converts the glucoses into alcohols $C_6H_{14}O_6$, dextrose yielding sorbitol and mannitol, and galactose forming dulcitol. Secondary hexyliodide, a derivative of normal hexane, is formed by the action of hydrogen iodide; hence the glucoses must possess all their six carbon atoms united in normal chain.

Dextrose on oxidation yields, in the first place, gluconic acid $C_5H_6(OH)_5 \cdot CO_2H$ which retains all its carbons and, like dextrose, forms a pentacetyl ester. Further oxidation converts it into saccharic acid $C_6H_{10}O_8$. Galactose behaves similarly, yielding the isomeric galactonic, and mucic acids. Taking further into consideration the reducing power of dextrose, the constitutional formula may be written:

$$CH_2(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CHO$$
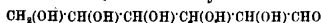
This formula does not fully express the behaviour of dextrose, which lacks many of the well-attested properties of the aldehydes; for example, it is not oxidised in the air, and does not show their various colour reactions. Tollens, in 1883, therefore, proposed the lactonic or γ-oxide formula (i.), which may also be written (ii.):
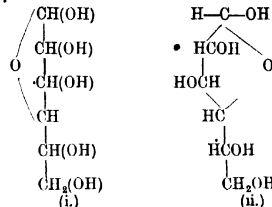
This formula (i. or ii.) is in entire agreement with the reactions of dextrose, and has been generally adopted. It is supposed that in presence of alkalis and other reagents the γ-oxide ring opens, forming the aldehyde.

The discovery of a third methyl glucoside (Fischer, Ber. 1914, 47, 1980) and of additional isomerides of other glucose derivatives (Hudson, J. Amer. Chem. Soc. 1915, 37, 1589, 1591; 1916, 38, 1223) has involved the recognition of a different internal linking in the sugar molecule. The oxygen atom may connect other pairs of atoms as well as the 1st and 4th. The new form of sugar termed γ-glucose (dextrose) obtained from this glucoside has not been isolated in the free state, but its tetramethyl derivative is known (Irvine, Chem. Soc. Trans. 1915, 107, 524). This is far more reactive than the corresponding derivatives of α- or β-dextrose: it condenses with alcohol with extreme ease and instantly reduces alkaline permanganate solution, giving rise to a new form of tetramethyl gluconic acid.

The work of Tanret (Compt. rend. 120, 1060) has shown that dextrose exists in more than one form. In addition to the hydrated and anhydrous modifications, he isolated two other anhydrous modifications. These differed particularly in optical rotatory power. Tanret described as α-dextrose having $[\alpha]_D + 110°$ when first dissolved, and falling in aqueous solution; a β-dextrose having $[\alpha]_D + 19°$, and increasing in solution; and a dextrose having $[\alpha]_D + 52.5°$, and remaining constant in solution. This modification was called γ-dextrose by Tanret. It is not the same, of course, as the γ-glucose mentioned above. It had long been known that the optical rotatory power of freshly dissolved dextrose diminished to about one-half its initial value in solution, and the term *mutarotation* or *bi-rotation* was applied to this phenomenon.

Dubrunfaut ascribed the change to purely physical causes. Fischer considered that the aldehyde dextrose underwent hydration to an alcohol $C_6H_{14}O_7$, of lower rotatory power. In view of Tanret's discoveries, it is now considered that the change in rotatory power is due to the mutual interconversion of the α- and β-dextroses, until equilibrium is attained. Tanret's γ-dextrose represents such an equilibrium mixture. It is

supposed that both α and β-dextrose have a closed γ-oxide ring structure, and it is still a matter of controversy whether some proportion of open-chain aldehyde is present in solution in the equilibrium mixture. (For the full discussion of this question, *see* E. F. Armstrong's The Simple Carbohydrates, Longmans, 1919).

To understand fully the relation of α- to β-dextrose, it is necessary to refer to the van't Hoff-Le Bel conception of space isomerism. Chemical compounds which rotate the plane of polarised light contain an *asymmetric carbon atom*, that is, one in which the four affinities are satisfied by four distinct radicals. Such a carbon atom is considered as lying in the centre of a tetrahedron, and each of the four different radicals with which it is combined as being at the four solid angles thereof. Two modifications of the compound are possible, which are related to one another like an object and its reflected image.

In the Tollens formula for dextrose, the carbon atom (C) has the four different groups, H, OH, the oxygen of the ring, and the complex $C_5H_{10}O_4$ attached to it. It is asymmetric, and two isomerides are possible, which are represented on a plane surface by writing H and OH on one or other side of the carbon atom, as the following formulæ show :—
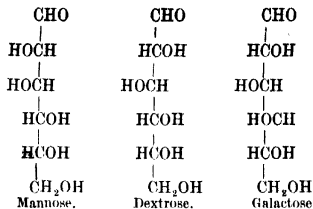
$$HO-C-H \qquad H-C-OH$$

a-Dextrose   β-Dextrose
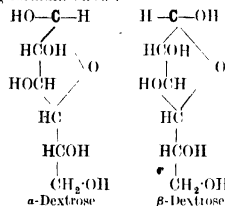
Corresponding to these two isomeric forms, dextrose gives rise to a double series of derivatives.

The compound represented by the formula

$$CH_2(OH)\overset{*}{C}H(OH)\overset{*}{C}H(OH)\ \overset{*}{C}H(OH)\overset{*}{C}H(OH)\ CHO$$

contains four asymmetric carbon atoms (marked *), and should, therefore, be capable of existing in 16 stereoisomeric forms, 8 of which would be mirror images of the other 8, and of equal but opposite rotatory power.

The carbohydrate group has afforded a unique opportunity of testing this hypothesis, and although only three of the isomerides occur naturally, no less than 12 have been prepared artificially by Fischer, who has, in addition, made them in such ways that their structure is established.
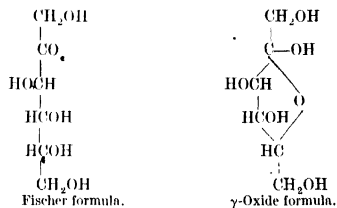
The known aldohexoses are the dextro- and lævo- isomerides of mannose, dextrose, idose, gulose, galactose, and talose. Two further isomerides, namely, *d*-allose and *d*-altrose, were obtained by Levene and Jacobs in 1910 (Ber. 43, 3141), starting from *d*-ribose. This is a component of many nucleosides, and so a considerable quantity had been accumulated for the purpose of applying the cyanohydrin process. It will suffice to give the constitutional formulæ as established by Fischer of the natural members :—

CHO	CHO	CHO
HOCH	HCOH	HCOH
HOCH	HOCH	HOCH
HCOH	HCOH	HOCH
HCOH	HCOH	HCOH
CH₂OH	CH₂OH	CH₂OH
Mannose.	Dextrose.	Galactose.

Mannose and galactose, like dextrose, exist in α- and β- forms, and it is more correct to write their formulæ in the form adopted for α- and β-dextrose.

As is to be expected, the isomeric glucoses differ but little in their chemical behaviour.

Formula of Lævulose.—Lævulose, when oxidised, forms glycollic and trihydroxyglutaric acid, or other acids with less than 6 carbon atoms. It forms an additive compound with hydrogencyanide, which yields lævulose carboxylic acid $C_7H_{14}O_8$ on hydrolysis ; and this, when boiled with hydriodic acid, is converted into methylbutylacetic acid $C_4H_9·CHMe·CO_2H$. Thus behaviour establishes lævulose as a ketohexose. It has the formulæ :

| CH₂OH	CH₂OH
CO	C—OH
HOCH	HOCH
HCOH	HCOH
HCOH	HC
CH₂OH	CH₂OH
Fischer formula.	γ-Oxide formula.

Fructose shows a pronounced tendency to exist in reactive forms other than the normal γ-oxide type—probably many of its compounds, including sucrose, are derived from the ethylene oxide type

$$OH·CH_2·[CH·OH]_2·CH·C(OH)·CH_2·OH$$
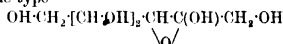
The ethylene oxide form of methyl fructoside readily condenses with acetone and rapidly reduces permanganate.

Formulæ of the Pentoses and Tetroses.—Eight aldopentoses are possible, of which seven have been artificially prepared, viz. *d*- and *l*-arabinose and xylose, *d*-lyxose, and *d*- and *l*-ribose. The two most common naturally occurring pentoses have the constitutional formulæ :

| CHO	CHO
HCOH	HCOH
HOCH	HOCH
HOCH	HCOH
CH₂OH	CH₂OH
l-Arabinose.	*l*-Xylose.
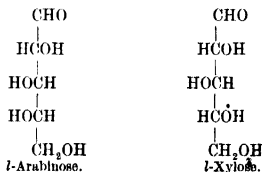
Like dextrose, they occur in two forms, and are more correctly written with a γ-oxide structure. A pentose believed to be *d*-arabinose has been isolated from the glucoside barbaloin

(Léger). Levene (Ber. 1909, 42, 3247 ; 1910, 43, 3147) obtained d-ribose from nucleic acid.

Three out of the four possible aldotetroses are known, viz. d- and l-erythrose and l-threose, but they have not been found in nature.

Reaction with Phenylhydrazine.—The behaviour of the carbohydrates with phenylhydrazine is particularly characteristic, and it has further an historical interest, as phenylhydrazine, in the hands of Fischer, served as one of the chief aids in the elucidation of the relationships of the group.

Dextrose reacts with the reagent in acetic acid solution in two stages. In the cold a phenylhydrazone is formed :

$$C_6H_{12}O_6 + C_6H_5 \cdot NH \cdot NH_2$$
$$= C_5H_{11}O_5 \cdot CH : N \cdot NH \cdot C_6H_5 + H_2O$$
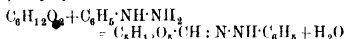
This is a colourless substance, soluble in water, and is obtained in two modifications, one or the other predominating according to the method of preparation. Similar compounds, with asymmetrically disubstituted hydrazines— for example, benzylphenylhydrazine—are often less soluble and more characteristic. Mannose is remarkable in forming an almost insoluble phenylhydrazone. The hydrazones of lactose and maltose are very soluble.

At the temperature of boiling water, dextrose reacts with excess of phenylhydrazine to form the phenylosazone

$$CH_2(OH) \cdot [CH(OH)]_3 \cdot C(: N \cdot NHPh) \cdot CH : N \cdot NHPh$$
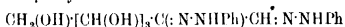
Dextrose (1 molecule) is heated with 3–4 molecules of phenylhydrazine, which should be almost colourless, and free from oxidation products, and an equal volume of 50 p.c. acetic acid in a flask immersed in boiling water for an hour or more. Usually the osazone begins to separate in 20 minutes or less. In the case of the disaccharides, no separation of osazone takes place from the hot solution.

The yellow osazone is filtered and carefully washed ; it may be crystallised from most organic solvents, but the most suitable appears to be a dilute solution of pyridine. Dextrose, mannose and lævulose form the same phenyl osazone, as they differ only in the relative positions of groups which are destroyed in the formation of the osazone.

Too much dependence must not be placed on the melting-points of the osazones in identifying unknown sugars in solution, as these depend very largely on the rate of heating, and the method of purification adopted. Disubstituted hydrazines do not directly form osazones with dextrose, though these may be prepared from the osones.

Diphenylmethanedimethyldihydrazine

$$CH_2(C_6H_4 \cdot NMe \cdot NH_2)_2$$

(J. von Braun, Ber. 1917, 50, 42 ; Votoček, Ber. 1917, 50, 35) appears likely to be of use in determining the configuration of aldoses. Hydrazones are only produced when at least two of the CH(OH) groups following the aldehyde group have the same spatial arrangements. Thus hydrazones are formed with arabinose, lyxose, rhamnose, ribose, rhodeose, fucose, galactose, mannose, but not with xylose, isorhodeose and glucose.

To recover the original sugar from the phenylhydrazone, it is boiled in water with a slight excess of benzaldehyde. The phenylhydrazine is removed as benzaldehyde phenylhydrazone, the excess of aldehyde extracted by ether, and the sugar solution concentrated *in vacuô*. With the disubstituted hydrazones better results are obtained on using formaldehyde.

The phenylhydrazine residues may be removed from the osazones by heating with fuming hydrochloric acid. Compounds termed osones are formed :
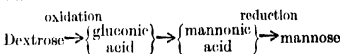
$$CH_2(OH) \cdot [CH \cdot (OH)]_3 \cdot CO \cdot CHO$$
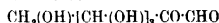
These are colourless syrups ; they act as strong reducing agents, combine directly with phenylhydrazine, and are non-fermentable. The slightly soluble osazones of the disaccharides, and of the pentoses, are converted into osones on boiling with benzaldehyde.

When reduced by means of sodium amalgam, the osones are converted into ketoses, and not into the aldoses from which they were formed. Thus it is possible to pass from dextrose to lævulose—a transformation of great importance —the stages being :
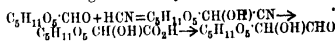
dextrose → phenylosazone → osone → lævulose
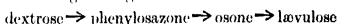
Another important transformation is that from dextrose to mannose, which is based on the fact that gluconic acid (q.v.), when heated with quinoline, is converted into a mixture of gluconic and mannonic acids. The stages in this case are :

$$\text{Dextrose} \xrightarrow{\text{oxidation}} \left\{ \begin{array}{c} \text{gluconic} \\ \text{acid} \end{array} \right\} \xrightarrow{\text{reduction}} \left\{ \begin{array}{c} \text{mannonic} \\ \text{acid} \end{array} \right\} \rightarrow \text{mannose}$$

By the aid of these two reactions, Fischer was able to pass from the synthetical α-acrose to d-glucose, d-fructose, and d-mannose, and so effect the complete synthesis of the naturally occurring hexoses.

The scheme on next page shows the successive operations.

Cyanohydrin synthesis.—The aldoses combine directly with hydrogen cyanide, forming nitriles, which, when hydrolysed, give rise to acids containing one carbon atom more than the original carbohydrate. The lactones of these acids, when reduced with sodium amalgam, yield the corresponding aldoses with one carbon atom more than the original carbohydrate :
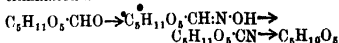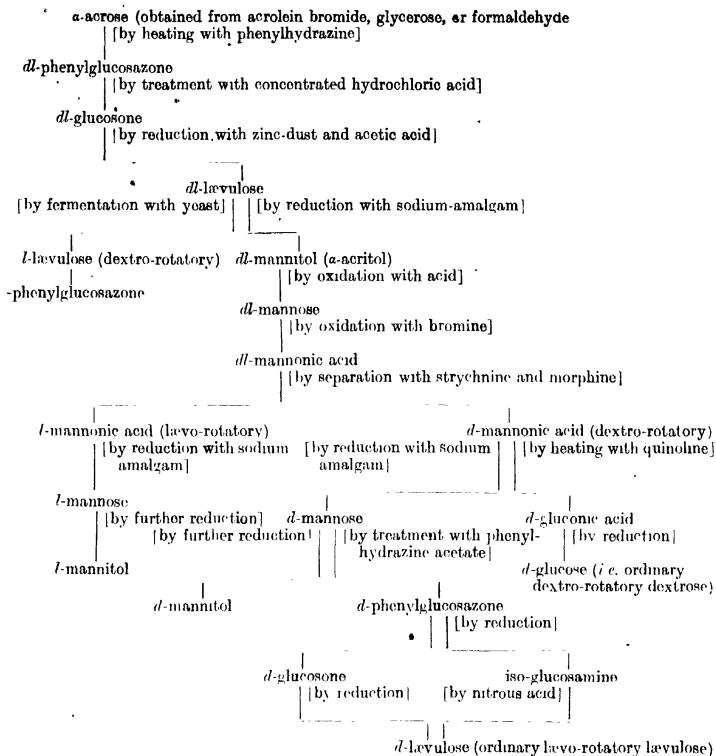
$$C_5H_{11}O_5 \cdot CHO + HCN = C_5H_{11}O_5 \cdot CH(OH) \cdot CN \rightarrow$$
$$C_5H_{11}O_5 \cdot CH(OH)CO_2H \rightarrow C_5H_{11}O_5 \cdot CH(OH)CHO$$

In this manner arabinose is converted into dextrose, dextrose into glucoheptose. Fischer has continued the process as far as the aldononose.

Actually two isomerides are formed at each stage, and arabinose gives both dextrose and mannose.

Degradation.—The converse change from dextrose to arabinose has been effected by several different methods.

Wohl (Ber. 1893, 26, 730, &c.) heated dextrose oxime with concentrated sodium hydroxide, so converting it into gluconic acid nitrile, from which, on further heating hydrogen cyanide was eliminated and d-arabinose formed

$$C_5H_{11}O_5 \cdot CHO \rightarrow C_5H_{11}O_5 \cdot CH:N \cdot OH \rightarrow$$
$$C_5H_{11}O_5 \cdot CN \rightarrow C_5H_{10}O_5$$

a-acrose (obtained from acrolein bromide, glycerose, or formaldehyde
| [by heating with phenylhydrazine]

dl-phenylglucosazone
| [by treatment with concentrated hydrochloric acid]

dl-glucosone
| [by reduction with zinc-dust and acetic acid]

dl-lævulose
[by fermentation with yeast] | | [by reduction with sodium-amalgam]

l-lævulose (dextro-rotatory)   *dl*-mannitol (*a*-acritol)
| | [by oxidation with acid]
-phenylglucosazone

dl-mannose
| [by oxidation with bromine]

dl-mannonic acid
| [by separation with strychnine and morphine]

l-mannonic acid (lævo-rotatory)   *d*-mannonic acid (dextro-rotatory)
| [by reduction with sodium   [by reduction with sodium | | [by heating with quinoline]
amalgam]   amalgam]

l-mannose |
| [by further reduction]   *d*-mannose   *d*-gluconic acid
| [by further reduction] | | [by treatment with phenyl- | [by reduction]
l-mannitol   hydrazine acetate]
| | *d*-glucose (*i e.* ordinary
| | dextro-rotatory dextrose)
d-mannitol   *d*-phenylglucosazone
| | [by reduction]

d-glucosone   iso-glucosamine
| [by reduction]   [by nitrous acid] |

d-lævulose (ordinary lævo-rotatory lævulose)

In practice the method adopted is to heat the oxime with acetic anhydride and a grain of zinc chloride ; a vigorous reaction ensues, and the pentacetate of gluconic acid nitrile is formed, from which hydrogen cyanide is eliminated by treatment with ammoniacal silver oxide.

Ruff (Ber. 1898, 31, 1573) oxidises the calcium salt of gluconic acid, with hydrogen peroxide in presence of a ferrous salt (Fenton's method). The carboxyl-group is eliminated, and arabinose formed.

Neuberg (Biochem. Zeitsch. 1908, 7, 527) effects the elimination of the elements of formic acid from gluconic and similar acids by electrolysis.

Weerman (Chem. Soc. Abstr. 1915, i. 387) obtains gluconamide by saturating gluconolactone in alcoholic solution with ammonia. On subsequent treatment with hypochlorous acid the amide is decomposed according to the scheme

$$R \cdot CH(OH) \cdot CO.NH_2 \rightarrow R \cdot CH(OH) \cdot N : C : O \rightarrow$$
$$R \cdot CHO$$
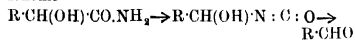
According to Irvine the reactions proceed with the utmost smoothness and constitute a great improvement on the methods hitherto in use.

The reaction has been applied to glucose, galactose, *l*-mannose and *l*-arabinose.

Action of Acids.—Dilute acids are without action on the aldoses, but when submitted to the continued action of acids, hexoses yield lævulic acid (acetopropionic acid)

$$(CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H)$$
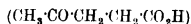
and formic acid, together with brown or black humus substances. The first product from the 2-ketohexoses is 4-hydroxymethylfurfuraldehyde

$$CHO \cdot C : CH \cdot CH : C \cdot CH_2OH$$
$$\underline{\qquad O \qquad}$$
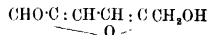
and it is to the condensation products of this aldehyde that the colour reactions of the ketoses with phenols are due. Blanksma and Ekenstein have shown that this aldehyde is also produced on heating mannose or dextrose with oxalic acid, and Fenton obtained 4-halogenmethylfurfurol from lævulose, and more slowly from the aldoses, on treatment with dry halogen hydride. The aldoses apparently undergo a 1-, 2-enolisation and conversion into 2-ketohexose.

Action of Alkalis.—Although absolutely stable in pure aqueous solution, dextrose, mannose,

and fructose pass over into one, another in presence of traces of alkalis in the cold. The optical rotation of a dextrose solution containing alkali, for example, slowly falls to zero. This change was observed by Lobry de Bruyn and Alberda van Ekenstein (Rec. trav. Chim. 1895, 14, 156, 204). It is due to the conversion of the sugar originally present into enol :

$$CH_2(OH)\cdot[CH(OH)]_3\cdot C(OH) : CH(OH)$$
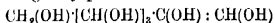
which is reconverted into all three hexoses.

Guanidine (Morrell and Bellars, Chem. Soc. Trans. 1907, 91, 1010–1033) brings about similar changes.

The action of alkalis on the carbohydrates is exceedingly complicated, and leads to the formation of a great variety of substances, in addition to humus compounds. The concentration of the alkali is of great importance, a larger number of products being formed when the relatively sparingly soluble lime and bartya (Kiliani) are used, than when concentrated sodium hydroxide is employed (Nef, Annalen, 1910, 376, 1 : 1914, 403, 204). The latter paper contains a summary of many years' work, and is the main source of information on this complex subject. In contact with dilute alkalis protound changes ensue in a hexose, an equilibrium being finally established between the various enolic forms. The number of possible forms is diminished as the concentration of the alkali is reduced. The unsaturated molecules formed undergo fission at the double bond.

The decomposition takes place quickly on heating, slower in the cold, with the production of acetol, acetone, lactic, acetic and formic acids, also glucinic and saccharumic acids, and other substances. With calcium hydroxide saccharin or calcium saccharinate is produced.

In addition to these substances, intermediate products are formed, more closely related to the monosaccharides, and from which these are reconstructed by the synthetic action of the alkali. It is established that hexoses break down into a molecule each of diose and aldotetrose, or into 2 molecules of glycerine aldehyde, that is, the 2 : 3 and 3 : 4-dienols decompose. The 1 : 2-dienols never break down into aldopentose and form aldehyde. Conversely, hexoses are never built up from pentoses.

Pentoses form 1 : 2-dienols, which, in the main, give aldotetroses and hydroxymethylene on decomposition ; they also form 2 : 3-dienols, breaking down to diose and glycerine aldehyde.

Dextroses exclusively form 2 : 3-dienols, breaking down to 2 molecules of diose ; they never give 1 : 2-dienols yielding hydroxymethylene and glycerine aldehyde. The strongly dissociated zinc hydroxide ammonia acts on the monosaccharides in the cold, producing methyl-glyoxaline

$$\begin{array}{c} CMc\cdot NH \\ \| \quad \quad\Ch \\ CH\cdot N \end{array}$$ (Windaus, Ber. 1905, 38, 1166 ; 1906, 39, 3886 ; 1197, 40, 799).

Saccharinic acids. According to Nef (Annalen, 1910, 376, 1) there are 24 isomeric saccharinic acids, with 6 carbon atoms, namely α-meta-saccharinic acids (αγδ-tetrahydroxy-hexoic acids).

$$CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2OH$$

derived from the 16 aldohexoses ; 4 isosacchar-

inic acids (α-hydroxymethyl αγδ-trihydroxy-valeric acids) :

$$CO_2H\cdot C(OH)(CH_2\cdot OH)\cdot CH_2\cdot CH(OH)\cdot CH_2(OH)$$
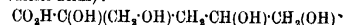
derived from the 8 β-ketohexoses ; 8 saccharinic acids (α-methyltetrahydroxyvaleric acids) :

$$CO_2H\cdot CMc(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2(OH)$$
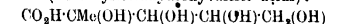
derived from the 8 γ-ketohexoses ; and 4 para-saccharinic acids (α, ω-hydroxyethyltrihydroxy-butyric acid) :

$$CH_2(OH)\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2(OH)$$
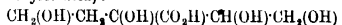
The lactones of these acids are known as saccharins. They give rise to characteristic alkaloid salts and phenylhydrazides, and possess optical activity. The saccharins are obtained by the action of lime on dextrose, maltose, or lactose.

Synthesis of Monosaccharides.—The condensation of formaldehyde under the influence of bases to carbohydrates has been the subject of repeated study. Butlerow, using milk of lime, obtained an uncrystallisable syrup with a sweet taste, which behaved as a sugar, but was non-fermentable and optically inactive. He termed the product methylentan. Loew improved the technique of the method by saturating a 4 p.c. solution of formaldehyde with slaked lime in the cold, and allowing it to stand. The syrupy product was termed 'formose,' and supposed by Loew to be homogeneous, but subsequently Fischer showed that on treating it with phenyl-hydrazine, a mixture of osazones was formed, one of which was identical with α-acrosazone. Nef has given reasons for believing formose (prepared by means of lead oxide) to be a mixture in approximately equal parts of isomeric hexoses and pentoses : its composition obviously depends on the alkali employed and its concentration.

Fischer and Tafel effected the condensation of acrolein dibromide by means of baryta, and showed the syrupy product to consist of two sugars, distinguished as α- and β-acrose. Subsequently, crude glycerose was made the starting-point of the synthesis. It is a mixture of glycerine aldehyde and dihydroxy acetone, both of which substances have, in after-years, been separately used as the initial material. Fenton has used glycollic aldehyde in the same manner.

A product of synthesis by all these methods is α-acrose, which is partly fermentable by yeast, and this Fischer isolated as phenylosazone, and showed to be identical with inactive dl-lævulose. From this by the series of reactions already given, he obtained the natural d-glucose, d-mannose, and d-fructose (lævulose), as well as their optical antipodes and a number of new isomerides. The application of the methods of degradation, elsewhere described, enabled pentoses and tetroses to be synthetically prepared from these hexoses, whilst the cyanohydrin reaction made it possible to obtain monosaccharides with 7, 8, and 9 carbon atoms.

The full explanation of the synthesis of carbohydrates in the green leaves of growing plants has still to be given. It is generally supposed that formaldehyde, the first product of assimilation, undergoes polymerisation to carbohydrates, a theory advanced by Baeyer in 1870 (Ber. 3, 63). Various compounds, such as glycollic and glyceric aldehydes and dihydroxy

acetone, have been suggested as intermediate stages in the polymerisation, but it has never been possible to detect any of these in the plant. Apparently the synthesis is asymmetric, hexoses of the dextro- series, and their polysaccharides being the only products of assimilation. It is supposed that the formaldehyde elements are superposed under the influence of the asymmetry of the protoplasm molecule, according to a definite plan, and are split off when six are united.

Synthesis of Disaccharides.—Though often attempted, the synthesis of disaccharides, by purely chemical means, has only been partially successful. Fischer and Armstrong have prepared a syrupy compound, probably identical with the natural sugar melibiose, by the interaction of acetochlorogalactose with sodium glucosate.

Fischer and Delbrück found that when acetobromoglucose is shaken in dry ethereal solution with silver carbonate and traces of water, the octacetyl derivative of a disaccharide is obtained. This is hydrolysed by cold barium hydroxide to a non-reducing disaccharide of the type of trehalose. The octacetyl- derivative is a mixture of isomerides, and yields isomeric disaccharides.

In the plant the di accharides are formed from hexose by the agency of enzymes, which exercise synthetic as well as analytic functions. It is undecided whether the same enzyme can cause both synthesis and hydrolysis, or whether special enzymes alone act as synthetic agents It is proved, however, that an enzyme effects the synthesis of a carbohydrate isomeric with that which it normally hydrolyses, the two compounds being apparently related in the same manner as the α- and β-methyl glucosides (*v.* Croft Hill, Chem. Soc. Trans. 1898, 73, 634 ; 1903, 83, 587 ; E. F. Armstrong, Proc. Roy. Soc. 1905, 76, B, 592 ; and monograph on Carbohydrates, 1919).

It has been established by Bourquelot that the equilibrium between a sugar and a glucoside when in contact with the appropriate enzyme can be displaced in the direction of the glucoside when the solvent contains excess of the hydroxy component of the glucoside. A large number of glucosides have been synthesised by Bourquelot from sugars dissolved in alcohols containing varying amounts of water : in every case the glucoside synthesised being that normally hydrolysed. This reaction, however, is not on all fours with that taking place in a concentrated solution of sugar in the absence of an alcohol, and so far all attempts to synthesise maltose or sucrose in this manner have been definitely without result.

In the following pages the occurrence, preparation, properties, and derivatives of the natural, mono-, di-, tri-, and tetra-saccharides, also glycogen and inulin, are dealt with. Sucrose, the dextrins, starch, and cellulose, are described in separate articles.

Dextrose. Dextroglucose, grape sugar, starch sugar $C_6H_{12}O_6$ and $C_6H_{12}O_2,H_2O$.

Occurrence.—Reducing sugars are very widely distributed in nature, but dextrose is almost always accompanied by lævulose, the two hexoses being probably derived from sucrose. It is thus found in honey, in the juice of most

fruits, and generally in vegetable tissues in small quantities. In the animal kingdom it is found in blood and in diabetic urine.

Formation.—Dextrose is formed on hydrolysing most of the known polysaccharides and glucosides, either with acids or enzymes ; it is similarly formed from glycogen. Thus cellulose, starch, dextrins, the disaccharides maltose, lactose, and sucrose, all yield dextrose.

Preparation.—Dextrose is usually prepared from starch or sucrose. It can be obtained from any of the substances mentioned, but they are less suited for the preparation in quantity.

Crude commercial dextrose is purified by dissolving in 8-10 p.c. of hot water, and adding dry boiling methyl alcohol, until a cloud is produced. This solution may be decolourised by shaking with animal charcoal, and filtering. On standing, anhydrous dextrose in a pure state separates abundantly. To prepare dextrose from sucrose, the latter must first be inverted. This is best effected by treatment at a temperature not exceeding 50°, with a small quantity of invertase or of pressed yeast. After a few hours the solution is evaporated *in vacuo* to a syrup, which solidifies on standing. The mass is washed with cold ethyl alcohol (sp.gr. 0·830), and the residue dissolved in more alcohol. Dextrose crystallises on cooling.

Sulphuric acid may be used for inversion ; it must be neutralised with baryta before evaporation. Soxhlet advises the use of alcoholic hydrochloric acid at 50° for 2 hours. Dextrose crystallises in a few days without neutralisation.

Properties.—Dextrose crystallises from strong (93-95 p.c.) ethyl or methyl alcohol in the anhydrous state, $C_6H_{12}O_6$, and from concentrated aqueous solutions at 30°-35° ; with special treatment, crystals of this composition may also be obtained. The crystals formed in aqueous solutions at ordinary temperatures contain a molecule of water of crystallisation, $C_6H_{12}O_6,H_2O$. The anhydride forms white crystalline crusts or powder and, when it separates from the solvent slowly, fairly well-defined glassy prisms ; the hydrate crystallises in cauliflower-like masses, but with care and slow crystallisation well-defined crystals can be obtained. Both bodies dissolve easily in water, the anhydride with evolution of heat. The hydrate dissolves freely in strong ethyl or methyl alcohol, especially on the application of heat, but the anhydride is practically insoluble in these liquids.

α-Dextrose exists in contact with boiling saturated alcoholic solutions : it forms hard brittle needles. From aqueous solutions monohydrate crystallises in six sided leaflets. As purified by crystallisation from dilute methyl alcohol a mixture of the different forms is obtained. A homogenous product is obtained by allowing the mixture to soak several days or weeks at a constant temperature with the solvent until the whole of the β-sugar present has been converted into the α-isomeride. Hudson and Dale (J. Amer. Chem. Soc. 1917, 39, 320) obtain the α-form by dissolving two parts of sugar in one part of water and adding 4 parts of glacial acetic acid, crystallisation being allowed to take place at the ordinary temperature.

β-Dextrose is formed by heating dextrose at

105°-110° for some hours or by crystallisation from water above 98°. From a solution in boiling pyridine a monopyridine salt separates which on exposure rapidly loses pyridine (Behrend). An even better method of preparation is said to be the following (Hudson and Dale): 10 parts of dextrose are dissolved in 1 part of water on a water bath, and 12 parts of glacial acetic acid heated to 100° are added. The whole is well mixed and removed from the water bath when crystallisation at once commences. After four such crystallisations pure β-dextrose is obtained.

γ-*Dextrose* (the equilibrium mixture) is obtained on precipitating with alcohol a concentrated aqueous solution which has stood for some time.

The initial optical rotatory powers of the two forms and that of the equilibrium mixture are as follows in aqueous solution :—

$$\alpha - [\alpha]_D + 113\cdot4°$$
$$\beta - [\alpha]_D + 19\cdot0°$$
$$\gamma - [\alpha]_D + 52\cdot2°$$

(Hudson and Dale, J. Amer. Chem. Soc. 1917, 39, 320).

An aqueous solution of dextrose containing 10 grams anhydrous dextrose in 100 c.c. of solution at 15·5°, has a sp.gr. 1·0385. Its solutions are optically active, i.e. possess the power of rotating the plane of polarisation of a ray of polarised light. The rotation is right-handed. Hesse (Annalen, 176, 106) and Tollens (Ber. 17, 2234) have carefully determined this constant, and the latter's results are expressed by the formula

$$[\alpha]_D = 52\cdot5° + 0\cdot018796P + 0\cdot00051683P^2$$

for the dry sugar, and

$$[\alpha]_D = 47\cdot73° + 0\cdot015534P + 0\cdot0003883P^2$$

for the hydrate $C_6H_{12}O_6,H_2O$, in which P = the percentage of anhydride and hydrate in solution. In dealing with solutions containing 10 p.c. dry sugar, the factors $[\alpha]_D = 52\cdot7°$ and $[\alpha]_D = 58\cdot3°$ may be used. The optical activity of dextrose solution is not materially affected by temperature. The activity is nearly twice as great in freshly prepared solution, diminution taking place slowly in cold, but rapidly in boiling solutions, until the constant value is arrived at. It is only crystallised dextrose that exhibits this property of bi-rotation, as it is called, dextrose fused and allowed to solidify does not show it (Hesse, Annalen, 176, 113). The solution of dextrose in strong alcohol retains the power of bi-rotation.

When dextrose is heated to 170°, the elements of a molecule of water are eliminated, dextrosan (glycosan) $C_6H_{10}O_5$ being produced. If the temperature is increased, that body is caramelised and charred. Dextrosan is again converted into dextrose by digestion with water or dilute acids. It is a hygroscopic, dextro-rotatory, non-fermentable substance. If the temperature is raised to 200°, and maintained at that point for a little time, gas, water, and volatile acids are given off, and if the heating is continued without being increased until these products cease to be evolved, the brownish-black residue (caramelised mass) becomes gradually solid.

This substance is soluble in water, completely if the temperature was not too high, and constitutes the colouring matter used in wine, beer, cookery, &c. Should the heat be further continued so that the body is destructively distilled, carbon mon- and di-oxide, and methane are evolved, aldehyde, furfuraldehyde, acetone, propionic, acetic, and formic acids, furane and furfurol distil over, and a black carbonaceous mass is left. V. CARAMEL.

The action of alkalis and of acids on dextrose has been discussed elsewhere. When reduced by sodium amalgam, the main product (35-40 p.c.) is sorbitol ; some quantity of mannitol is also formed in alkaline, but not in neutral or acid solution. It is derived from the mannose produced by the action of alkali on dextrose.

Oxygen has no action on dextrose in neutral or acid solutions, but alkaline solutions absorb the gas. Ozone oxidises it to formic acid, saccharic acid, &c., being produced. Strong nitric acid converts dextrose into saccharic acid, and finally into oxalic, carbonic, and formic acids. Treated with chlorine or bromine in the presence of water, the resulting product yields gluconic acid when submitted to the action of silver oxide.

Dextrose in alkaline solutions reduces the oxides of gold, platinum, silver, mercury, bismuth, lead, copper, iron, manganese, &c. ; in the case of gold, platinum, silver, and mercury, the reduction is complete, the metal being formed ; in the other cases lower oxides are produced. Ferrocyanide of potassium, indigo, picric acid, litmus, and such substances are also reduced by dextrose in alkaline solution. The products from the dextrose are not the same in all cases, but they consist chiefly of carbonic, formic, oxalic, and glycollic acids, other products being also formed.

Nearly all the true yeasts (*Saccharomyces membranæfaciens* is an exception), a great number of torulæ, moulds, and other organisms ferment dextrose, yielding carbon dioxide and alcohol as the chief products. Glycerol, succinic acid, and other bodies (fusel oil) are formed at the same time, the proportions of these bodies varying materially with the organisms and the conditions under which the growth takes place. The work of Ehrlich suggests that most of these by-products are derived from amino-acids, produced from the yeast and not from dextrose (v. FERMENTATION).

Pressed yeast-juice, zymase, which contains no living protoplasm, also ferments dextrose.

In the presence of growing bacteria of various species, dextrose yields many products, one species converts it into lactic acid, another into butyric acid, another into cellulose, the so-called slimy fermentation, and so on. Other organisms oxidise dextrose (v. FERMENTATION).

Dextrose combines with sodium chloride, bromide, and iodide, forming well-defined crystalline compounds ; these decompose in aqueous solution. Compounds with bases are indefinite in character, and unstable. Sodium and potassium dextrosate $C_6H_{11}MO_6$ are obtained on adding sodium or potassium ethoxide to an alcoholic solution of dextrose. Several calciumdextrosates are described containing varying proportions of dextrose, lime, and water. Dextrose is not precipitated with lead

acetate, but basic lead salts are obtained in presence of ammonia.

The methylglucosides. These are of importance, as types both of glucosides generally, and of the two isomeric series of dextrose derivatives. They are regarded as stereoisomeric γ-oxides, and have the following structural formulæ :—

α-Methylglucoside   β-Methylglucoside
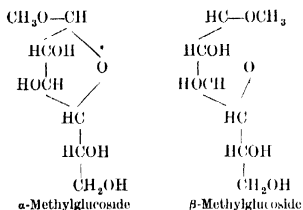
α-Methylglucoside crystallises in long needles, m.p. 165° [a]$_D$+157° ; β-methylglucoside forms rectangular prisms, m p. 104° [a]$_D$−33°.

They are hydrolysed by warm mineral acids to methyl alcohol and dextrose, the β-isomeride being attacked 1·8 times as rapidly as the α-isomeride. Each glucoside requires its own particular enzyme to hydrolyse it. α-Methylglucoside is hydrolysed by maltase alone ; β-methylglucoside only by emulsin. They are used as test materials in studying enzyme action.

The isomerides are both formed when dextrose is heated with methyl alcohol containing hydrogen chloride.

To obtain α-methylglucoside, 1 part of dextrose is heated with 4 parts methyl alcohol containing 0·25 p.c. hydrogen chloride, for 50 hours in an autoclave. The solution deposits crystals of the glucoside on evaporation, and the mother liquors, after further heating, give a second and third crystallisation, as the β-isomeride present is converted into the α- by the acid. A yield of 80 p.c. or more is obtained.

To obtain β-methylglucoside, solid anhydrous glucose is dissolved in methyl alcohol, nearly saturated with dry hydrogen chloride, at room temperature. As soon as etherification is complete, as witnessed by the absence of reducing power, the solution is neutralised and evaporated, and a mixture of α- and β-isomerides obtained in about equal quantities. The α- is partly separated by crystallisation from strong alcohol. The residue is dissolved in water, and fermented by a pure culture yeast. The α-methylglucoside is hydrolysed, and the dextrose fermented ; the β-methylglucoside remains untouched, and is recovered and purified.

In addition to the crystalline α- and β-methylglucosides obtained in the reaction between α-glucose and methyl alcohol containing 1 p.c. HCl, a considerable amount of syrup is formed which after distillation in a vacuum is an oil, $C_7H_{14}O_6$, b.p. 200°–215°/0·2 mm., [a]$_D$ −4°. It is named γ-methylglucoside to differentiate it from the α- and β-forms (E. Fischer, Ber. 1914, 47, 1980).

It is stable to alkalis, Fehling's solution or hot water, scarcely attacked by emulsin or by yeast extract at 37° C., but is hydrolysed to

glucose and methyl alcohol by dilute acetic acid at 100°, or by dilute hydrochloric acid at 100° or 18°.

The other carbohydrates form analogous methylglucosides, and similar compounds are obtained with ethyl alcohol. (For other artificial glucosides, v. GLUCOSIDES).

The methyl derivatives of the sugars have proved of great importance in the elucidation of their structure. Purdie and Irvine's method of methylation is employed, consisting in dissolving the sugar in methyl iodide and a little acetone and boiling the mixture with silver oxide. By protecting some of the hydroxyl groups from methylation those remaining may be methylated and the configuration thus established.

A very large number of dextrose compounds have been prepared, in some of which the aldehydic hydroxyl is concerned, whilst others, e.g. the acetates, involve all five hydroxyls. As already stated, in most cases two isomerides derived from α- and β-dextrose have been prepared. Few of these compounds are really characteristic of dextrose, and it must suffice in the space at disposal to indicate the properties of some of them in tabular form.

Compound	Appearance	M.p	[a]$_D$
Pentanitrate	amorphous	--	+98°
α-Pentacetate	colourless needles	112°–113°	+100°
β-Pentacetate	granular crystals	134°	+3°
α-Acetochlorodextrose	long needles	63°–64	
β-Acetochlorodextrose	stellate aggregates	73°–74°	+165°
α-Acetobromodextrose	prisms	79°–80°	
β-Acetobromodextrose	lustrous needles	88°–89°	+198°
α-Acetonitrodextrose	needles	92°	+1·5°
β-Acetonitrodextrose	lustrous rhombic prisms	150°–151°	+149°
Pentabenzoate	needles	179°	
Monomethyl-α-dextrose		161°	+108°
Monomethyl-β-dextrose		135	+24°
αβ-Dimethyl-α-dextrose		85°–87°	+82°
αβ-Dimethyl-β-dextrose		108°–110°	+6°
Trimethyldextroses	syrup		+79° −8°
Tetramethyl-α-dextrose	syrup	81°	+101°
Tetramethyl-β-dextrose		81°	+73°
Pentamethyldextrose	stellate crystals	42°–43°	−7°
Dextroseethylmercaptal	colourless matted needles	127°–128°	
α-chloralose	bunches of needles	186°	
β-chloralose	fatty plates	230°	
Dextrose diacetone	needles	107°–109°	
Dextrose ureide	rhombic plates and needles	207°	
Semicarbazone	needles	175°	
Thiosemicarbazone	rhombic plates	204°	
Anilide	needles	147°	
Oxime	needles	137°	
α-Phenylhydazone	needles	159°–160°	−70°
β-Phenylhydazone	needles	140°–141°	−5°
p-Bromophenylhydrazone		164–166	
Methylphenylhydrazone	colourless plates	180°	
α-Amylphenylhydrazone	light brown needles	128°	
α-Allylphenylhydrazone	light yellow needles	155°	

Compound	Appearance	M.p.
α-Benzylphenylhy-drazone	light yellow needles	165°
Diphenylhydrazone	colourless oblique prisms	161°
β-Naphthylhydrazone	brown needles	95°
Phenylosazone	aggregates of yellow needles	206°
p-Bromophenyl-osazone	yellow needles	222°
Nitrophenylosazone	reddish needles	257°
Dextrose-o-diaminobenzene	colourless lustrous needles	—
Didextrose-o-diaminobenzene	slender colourless needles	—
Dextrose-γ-diaminobenzoic acid	lustrous silver plates	243°

Since acetobromoglucose is the starting-point for many other glucose derivatives its preparation is given in detail. 200 grams powdered crystalline anhydrous glucose are heated on the water-bath with 100 grams of alcoholic sodium acetate and 1 litre of acetic anhydride for 2½ hours. The product is poured into 4 litres of ice water, and the crude β-penta-acetylglucose is recrystallised from 96 p.c. alcohol after freeing it from acetic anhydride by water (yield 74 p.c.).

150 grams of the penta-acetate are treated with the commercial solution of hydrobromic acid in glacial acetic acid (300 grams) for 2 hours at ordinary temperatures, 600 c.c. chloroform added and the whole poured into 2 litres of ice water. The chloroform layer is separated, and the rest shaken with 150 c.c. chloroform; the united chloroform extracts are washed with 1 litre of water, dried over calcium chloride, concentrated in a vacuum, and the residue gradually treated with light petroleum. The resulting crystals are rapidly recrystallised from 75 c.c. amyl alcohol, washed with light petroleum and stored in a vacuum desiccator over soda-lime. (*See* E. Fischer, Ber. 1916, 49, 584.)

The reduction of acetobromoglucose with zinc-dust and acetic acid yields the acetyl derivative of *glucal*,
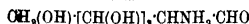
$$CH_2(OH)\cdot CH\cdot CH_2\cdot CH(OH)\cdot C=CH(OH)$$
$$|\underline{\qquad\quad -O\quad}|$$
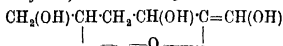
a soluble viscid syrup, b.p. 170°–180°/0·2 mm. Glucal can be further reduced by hydrogen and palladium to *hydroglucal*,

$$CH_2(OH)\cdot CH\cdot CH_2\cdot CH(OH)\cdot CH\cdot CH_2(OH)$$
$$|\underline{\qquad\qquad -O\quad}|$$
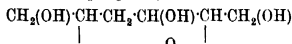
which melts at 86°–87°, tastes slightly sweet, and has $[\alpha]_D +16°$.

d-Glucosamine (Chitosamine) or amino-dextrose has the formula

$$CH_2(OH)\cdot[CH(OH)]_3\cdot CHNH_2\cdot CHO$$

It is obtained by boiling the shells of lobsters, particularly the claws, with concentrated hydrochloric acid, when the hydrochloride results. The shells of lobsters consist of carbonate of lime and chitin. Chitin is a constituent of various invertebrate skeletal structures, and of the cell walls of fungi; it is considered by Irvine to contain acetylamino-dextrose and amino-dextrose residues in the proportion of 3 to 1 $(C_{36}H_{50}O_{19}N_4)n$. It is prepared from the hydrochloride by decomposing it with

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diethylamine (Breuer, Ber. 1898, 31, 2193) or sodium methoxide (Lobry de Bruyn, *ibid.* 1898, 31, 2476). Fischer and Leuchs (Ber. 1903, 36, 24) effected the synthesis by the combination of *d*-arabinose and ammonium cyanide to *d*-glucosaminic acid, the lactone of which was reduced to *d*-glucosamine. Glucosamine forms a colourless crystalline powder, or long needles; m.p. 115° $[\alpha]_D +48°$. The aqueous solution reacts alkaline, but is stable. It is not fermentable. The pentacetate exists in two forms, needles, m.p. 183·5° and 133° respectively; the former is optically inactive, the latter has $[\alpha]_D +86·5°$. The oxime forms prisms, m.p. 127°. Two modifications of the hydrochloride are known: glistening monoclinic crystals $\{\alpha\}_D^{23} +100°$, falling to $+72·5°$ on standing, and hexagonal needles $[\alpha]_D^{2?}$ constant at 72·5°.

It cannot be converted into dextrose directly, though it gives dextrose phenylosazone when heated with phenylhydrazine. Irvine and Hynd (Chem. Soc. Trans. 1912, 101, 1128) have converted it into aminomethyl glucoside, and this by the action of baryta into methylglucoside and ultimately to *d*-glucose. When methylglucosamine is treated with sodium nitrite a mannose derivative is obtained almost quantitatively. Probably a Walden inversion takes place (*see* Chem. Soc. Trans. 1914, 105, 698). By the action of nitrous acid, a compound, $C_6H_{10}O_5$, is formed, which was at one time regarded as a carbohydrate, and termed chitose, but was shown by Fischer and Andreae (Ber. 36, 2587) to be a hydrated furfurane derivative

$$\begin{array}{c}CH(OH)\cdot CH(CHO)\\|\\CH(OH)\cdot CH(CH_2OH)\end{array}\!\!\!>\!\!O$$
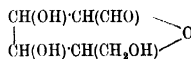
Chitose forms an oxime and phenylhydrazone and is oxidised by bromine to chitonic acid. Glucosamine was formerly regarded as a derivative of chitose, and termed chitosamine.

An isomeride of glucosamine is *iso*glucosamine $CH_2(OH)\cdot[CH\cdot(OH)]_3\cdot CO\cdot CH_2\cdot NH_2$, which Fischer obtained by reducing phenylglucosazone with zinc-dust, and which is converted by the action of nitrous acid into lævulose.

The glucosimines were formerly believed to be imino compounds, but Irvine, Thomson and Garrett (Chem. Soc. Trans. 1913, 103, 238) suggest that they are amino-glucosides. Levene (J. Biol. Chem. 1916, 24, 59) shows that the nitrogen content of glucosimine, galactosimine, xylosimine, and lyxosimine as given by (i) Kjeldahl's method, and (ii) by van Slyke's nitrous acid method indicates the presence of a primary amino group.

Chondrosamine (Levene, J. Biol. Chem. 1916, 26, 143) gives galactosazone, and is therefore probably a lyxohexosamine.

By condensing bromotriacetylglucosamine with hydroxy compounds in the presence of a base such as morphine, acetylated amino glucosides are obtained. The compounds formed are of two types: stable N-cyclic compounds and normal glucosides, such as α-aminohelicin and α-aminosalicin (Irvine and Hynd, Chem. Soc. Trans. 1913, 103, 4½).

A new glucosamine derivative, lycoperdin $C_{13}H_{24}O_9N_3$, has been isolated from the fungus

Lycoperdum gemmatum (Kotake and Sera, Zeitsch. physiol. Chem. 1913, 88, 56).

Manufacture of commercial dextrose—i.e. dextro-glucose, glucose, saccharum, ·saccharine, &c.—These products, varying much in character and composition, are all prepared by the action of acids on starch or starchy substances, such as rice, maize, &c., and when these latter are the raw material, it has been proposed to employ the combined action of diastase and acids. When starch is acted upon by dilute acids, it is dissolved, dextrins and maltose being produced. These bodies, by the further action of the acid, yield dextrose; this itself does not resist the action of acids, so that during the process of conversion, a portion of it is attacked, with the production of substances imperfectly studied (*v.* ISOMALTOSE).

The phases of the action of dilute acids on starch are easily followed. After heating has been continued for a short time, a portion of the solution cooled ceases to give a blue colouration with iodine ; this indicates absence of starch ; in the place of this a reddish-brown colouration is produced, this indicates the presence of a-dextrin. After a time this disappears, and at length the solution ceases to give a precipitate, when to a portion of it twice its bulk of alcohol (sp gr 0·820) is added, or when to a portion from which the sulphuric acid has been separated by baryta-ammoniacal lead acetate is added. This establishes the absence, not of maltose, but only of dextrin. For syrup the boiling is stopped as soon as the iodine test gives a port-wine colour ; for solid dextrose it is continued till alcohol causes no precipitate. The processes involve in the manufacture may be conveniently arranged as follows :—

    (*a*) The conversion.
    (*b*) The neutralisation.
    (*c*) The filtration.
    (*d*) The decolourisation.
    ( ) The concentration.
    (*f*) The purification.

(*a*) *The conversion.*—In this country the materials chiefly employed in the manufacture of commercial dextrose are sago, maize, and rice starch, finely ground rice itself, as well as granulated maize and rice being at times used. Potato starch is also used in Germany. In America green-maize starch is the chief material ; hence the term ' corn sugar.' The acid usually employed in Europe is sulphuric ; hydrochloric acid is generally used in America ; and nitric acid as well as a mixture of nitric and sulphuric acids have been recommended. The use of sulphurous and orthophosphoric acids has also been advocated. The proportions of material, water, and acid generally employed in the case of sulphuric acid are 100 : 250 : 5, and when green starch, *i.e.* undried purified starch, is used, 1½ parts are taken instead of 1 part dry starch. When pressure converters are used, the acid can be reduced to 0·5 p.c.

Formerly open converters made of wood, lined with lead and provided with steam coils of lead and stirring gear, were used, but these are now abandoned nearly everywhere for closed converters. These are made of cast iron, copper, or gun metal, and are worked at a pressure of 30 lbs. of steam.

The operations involved in the manufacture, whatever converter is used, are as follows : Half the sulphuric acid is mixed with half the water in a separate vat constructed as the converter, with or without coil, and at such a temperature that the heat of the dilute acid will be less than the gelatinising point of the starch of the material employed. This vat is furnished with stirring gear, and placed under a hopper, in which is stored the starch or starchy substance. When the dilute acid is at the right temperature, the material is allowed to flow into it, the stirring gear being kept in motion ; a milk of starch in dilute acid is thus obtained. Meanwhile the remaining half of the acid and water are introduced into the converter, and heated to boiling, then the starch milk is run in at such a rate that the temperature does not fall far below boiling, and the introduction should be effected as rapidly as possible.

The time required for conversion depends on the rate of introduction of the starch milk, and on the pressure employed, &c. For corn syrup an average time from the commencement of the starch introduction to the discharge is a little over an hour, for solid sugar about 1½ hours is required. When converted, the liquid is blown into the neutralising vats.

(*b*) *The neutralisation.*—Finely-ground chalk is used to neutralise the acid employed in the conversion. The chalk is converted into a milk with water, and gradually introduced into the converted liquid. About 12 lbs. of powdered chalk are taken for every 10 lbs. sulphuric acid employed ; this is more than the theoretical quantity, but it is found to answer in practice, owing, no doubt, to the insolubility of a portion of the chalk. The neutralised liquid is kept stirred for some time, and is then allowed to rest. It is found best to allow it to cool and settle gradually, and then draw off the clear portion ; but where vat room is a consideration, the neutralised liquid is run immediately to the filter presses (*v.* FILTRATION).

(*c*) (*d*) The clear filtered solution is passed through bone-char filters of the same construction as those described under SUGAR. Sulphurous acid is sometimes used in bleaching the product.

(*e*) *Concentration.*—This operation is effected in vacuum pans (*v.* SUGAR), and is considered complete when the syrup contains about 82 p.c. solid matter, *i.e.* reaches a sp.gr. of 1·50. It is then run into moulds, usually cone-shaped vessels, in which, on standing and cooling, it solidifies after a short time. This is hastened by the introduction of some previously solidified sugar. The solidified mass extracted from the mould by a short immersion in hot water is broken into irregular lumps, in which form it appears in the market. The colour of the commercial parcels varies from pure white to dark-brown ; this depends on the character of the material employed (the purity and variety of the starch), on the mode of conversion, and the extent to which the decolourisation was carried. The composition is also very variable, but the constituents in all are the same, viz. dextrose, maltose, dextrin, unfermentable organic bodies, and ash. Very few samples contain dextrin, some few maltose, and the proportion of unfermentable bodies varies very much, being sometimes as high as 15 p.c. The syrups,

which are used in confectionery, contain a large percentage of dextrin and maltose.

In the United States the conversion is carried out by stirring the green corn starch, made in the same factory, with a large body of water, and subjecting this mixture to a high heat under pressure, the process being a hydrolytic one. A small amount of pure hydrochloric acid is added to facilitate the catalytic action. The conversion is performed in large vessels 6 feet in diameter, and about 20 feet high, made of hammered copper 1 inch in thickness.

After the required conversion, the traces of acid are neutralised with soda ash, the mixture being left very slightly acid to litmus, and excess of alkali being very carefully avoided, as the least trace colours the liquid. In the case of glucose syrup, conversion is complete in less than 10 minutes; conversion into anhydrous dextrose takes considerably longer. The converted starch, now an almost white liquor, is run from the neutralisers through filter presses, to remove the dissolved gluten, &c., which is precipitated during neutralising, and then through an evaporator, which reduces the gravity to 30° B. It is then run successively over three bone-char filters, each 10 feet in diameter and 24 feet high, and containing 70,000 lbs. of bone-char each. The liquors receive a much greater amount of bone-char treatment than is the custom in sugar refineries, passing, in all, over 72 feet. The remaining traces of acid are completely neutralised, and the liquid has a brilliant crystal-white appearance. The bone-char is revivified after each bath. The liquor is concentrated in vacuum pans to the required density 42°–45° B., and crystallises on cooling. (A full account of the American industry of corn products is given by Wagner (J. Soc. Chem. Ind. 1909, 28, 343).)

The average composition of these products, according to the older analyses, is as follows :—

	Corn syrup	70 sugar	89 sugar	Anhydrous sugar
	P c.	P c	P.c.	P c.
Water .	19·0	19·7	11·2	4·0
Dextrose .	38·5	70·2	79·9	94·6
Dextrin .	42·0	9·3	8·0	0·7
Ash . .	0·5	0·8	0·9	0 7

The ash consists principally of chlorides. Wesener and Teller (J. Ind. Eng. Chem. 1916, 8, 1009) give the following analysis as representing the modern product :—

Water . . .	15–20 p.c.	
Proteins . .	about 0·06 p.c.	
Mineral matter .	Traces.	
Glucose . .	12–17 p.c.	
Maltose . .	16–23 p.c.	

and Dextrin (or dextrins) not fermented by yeast, but made fermentable by pancreatin, takadiastase, &c.

From which it appears that the proportion of maltose present generally exceeds that of dextrose. In the older analyses all the reducing sugar was regarded as dextrose.

(f) *Purification.*—Behr (Eng. Pat. 9797,

1884; 1767, 1885) manufactures pure commercial crystalline anhydrous dextrose by adding crystals of dextrose to a solution concentrated to 85 p.c., and allowing the mixture to stand at about 35°. After a short time an abundant crop of crystals separates, and by treatment in a centrifugal machine, the uncrystallised syrup is removed (v. Sugar).

In the older process of Soxhlet, the concentrated syrup was dissolved in about an equal weight of boiling methyl alcohol, and allowed to stand. The crystals were drained, and the loaves washed with methyl alcohol, which was recovered from the loaves and mother liquors by distillation in a vacuum.

Dextrose from Cellulose.—Cellulose is disintegrated by boiling with acids only with great difficulty, and at high temperatures, with the formation of dextrose, and the process cannot compete industrially with the preparation from starch. Numerous attempts have been made to obtain dextrose from wood cellulose, with the industrial objective of the manufacture of alcohol.

Simonsen (Zeitsch. angew. Chem. 1898, 195, 219, 962, 1007) found the most favourable conditions for the conversion of 40 grams of cellulose to be a digestion for 2 hours at 6–8 atmospheres, with 1000 c.c. of 0·5 p.c. sulphuric acid. 45 p.c. of reducing sugar was obtained, but, according to Korner (ibid. 1908, 2353), this is not all fermentable dextrose.

Ekström (Fr. Pat. 380358, July 29, 1907) treats sawdust with 95 p.c. sulphuric acid at the ordinary temperature for 20 minutes, dilutes to 1 p.c. free acid, and heats from 1 to 5 hours under a pressure of 3–8 atmospheres ; 55–57 p.c. conversion is claimed.

Ewen and Tomlinson (U.S. Pat. 938308, Oct. 26, 1909) heat sawdust with a minimum of 5 p.c. acid to a temperature between 135° and 162°. The use of 2–6 p.c. hydrofluoric acid has also been suggested (Orlowski, Fr. Pat. 405187, July 17, 1909).

*d-*Mannose $C_6H_{12}O_6$ occurs in nature in the form of anhydride-like condensation products, known as mannosans. It is best prepared from the vegetable ivory nut (*steinnuss*) which is used in Berlin and elsewhere for the manufacture of buttons and collar studs. The waste turnings are hydrolysed to mannose by boiling for 6 hours with 2 parts of hydrochloric acid. It was originally obtained by Fischer and Hirschberger by oxidising mannitol with nitric acid. Mannose is characterised by forming an insoluble yellow phenylhydrazone, m.p. 186°–188°, and use is made of this compound in isolating it from solution. The hydrazone is subsequently decomposed with benzaldehyde, or better, formaldehyde, and the resulting solution concentrated *in vacuo* till the sugar crystallises. It may even be isolated in the solid form without the intermediate formation of the phenyl hydrazone (Hudson and Sawyer, J. Amer. Chem. Soc. 1917, 39, 470).

Mannose separates in colourless rhombic crystals [*a : b : c*=0·319 : 1 : 0·826] of sweet taste, m.p. 132° ; sp.gr. 1·539. 100 c.c. of the saturated aqueous solution at 17·5° contain 24·8 grams ; in absolute alcohol it is almost insoluble. It shows muta-rotation, the equilibrium value being [*a*]+14·5°. The α-form has

$[a]_D + 34 \cdot 0°$, and the β-form $[a]_D - 17 \cdot 0°$ (Hudson and Dale, J. Amer. Chem. Soc. 1917, **39**, 320).

It is very similar to dextrose in all its properties, yielding the same phenylosazone. It is fermented by all yeasts which attack dextrose and lævulose. Bromine oxidises it to mannonic acid ; sodium amalgam reduces it to mannitol.

a-Methyl mannoside had m.p. 190°, $[a]_D^{20} + 80°$. The oxime crystallises in colourless needles, m.p. 167°–180°. Like the phenylhydrazone, the substituted hydrazones are all sparingly soluble.

Caroubinose, a carbohydrate isolated from the seeds of the carob bean, is identical with mannose.

d-**Galactose** $C_2H_{12}O_6$. Milk sugar, when hydrolysed by means of acids or enzymes, yields dextrose and galactose in equal proportions. On a commercial scale, sulphuric acid is used to effect hydrolysis under pressure at 105°, after which the solution is neutralised and concentrated until an amount which contained 500 grams of milk sugar weighs 640 grams. The syrup is set aside with a few crystals of galactose, and, after some days, the crystalline mass is washed with 80 p.c. alcohol, and the galactose purified by recrystallisation from aqueous alcohol. Even the very best commercial galactose contains minute quantities of dextrose ; to remove this it must be treated with a pure culture of some yeast, such as *S. Ludwigii*, which ferments dextrose, but not galactose.

Galactose is a constituent of raffinose and stachyose, and is widely distributed in the polymeric form, galactan, particularly in gums and seaweeds. It occurs in a few glucosides. It is a colourless crystalline powder, $+1H_2O$, m.p. 118°–120° (from water), anhydrous m.p. 165° (from alcohol), less soluble than dextrose, and has the same general properties as dextrose. The most characteristic behaviour is the formation of mucic acid on oxidation with nitric acid.

Galactose exhibits muta-rotation ; the a-isomeride has $[a]_D^{20} + 144°$, the β-modification $+52°$. The equilibrium value is $[a]_D^{20} + 80 \cdot 5°$. The influence of concentration and temperature on this value is expressed by the equation

$$[a]_D = 83 \cdot 883 + 0 \cdot 0785 p - 0 \cdot 209 t$$

where p and t denote concentration and temperature respectively.

Galactose derivatives are prepared similarly to the corresponding dextrose compounds. The a-pentanitrate (Will and Lenze, Ber. 31, 68) forms needles, m.p. 115°–116° ; the β-isomeride has m.p. 72°–73° ; the β-pentacetate has m.p. 142° ; a-methylgalactoside has m.p. 111°–112°, $[a]_D^{20} + 179 \cdot 3°$, and crystallises in transparent doubly refractive needles ; the β-isomeride forms needles, m.p. 173°–176°, $[a]_D^{20} + 2 \cdot 6°$; the phenylhydrazone has m.p. 158°, the phenylosazone when quickly heated melts at 193°–194°.

Galactose penta-acetate has been isolated in four forms :—
(i) m.p. 142°, $[a]_D + 25°$ (in chloroform), $+8°$ (in benzene) ;
(ii) m.p. 95·5°, $[a]_D + 107°$ (in chloroform) ;

(iii) m.p. 98°, $[a]_D - 42°$ (in chloroform) ;
(iv) m.p. 87°, $[a]_D + 61°$.

(Hudson and Parker, J. Amer. Chem. Soc. 1915, **37**, 1589, 1591 ; Hudson and Johnson, *ibid.* 1916, **38**, 1223).

Some yeasts ferment galactose, but not all those which ferment dextrose and lævulose. It is apparently possible to grow a yeast in presence of galactose and dextrose, until it acquires the power of fermenting galactose. Galactose is identical with the sugar cerebose, isolated from the brain by Thudichum, where it is a constituent of the cerebrosides, phrenosin and kerasin.

* **Lævulose** or d-**Fructose** $C_6H_{12}O_6$ is a keto-hexose or ketose sugar. It is found together with dextrose in honey and in many fruits, and, combined with dextrose, it occurs in sucrose, raffinose, stachyose, &c. Inulin, found in dahlia tubers is completely converted into fructose on hydrolysis. It has not so far been produced by the hydrolysis of any glucoside.

It is termed d-fructose, in spite of the lævo-rotation, to indicate that it belongs to the d-mannitol series

After prolonged heating at 165°–170°, cane sugar becomes converted into a mixture of lævulosan ($C_6H_{10}O_5$) and dextrose, without change of weight. On fermenting the aqueous solution of the mass with yeast, the dextrose is decomposed, while the lævulosan remains unchanged, and may afterwards be converted into lævulose by treatment with dilute acids.

Preparation.—It is best prepared from inulin. 100 grams of inulin with 1 p.c. ash are heated with 250 c.c. water and 0·5 gram hydrochloric acid for half an hour in a boiling water-bath, neutralised with 1·5 grams sodium carbonate evaporated on the water-bath at 60°, and finally over sulphuric acid *in vacuô* to a thick syrup. This is extracted with absolute alcohol, put aside for 24 hours, the solution poured off clear, and inoculated. Complete crystallisation of the lævulose is obtained in 3 days, and it is quite pure after one more crystallisation.

Inulin may also be hydrolysed with 0·5 vol. p.c. oxalic acid.

(For the preparation from Jerusalem artichokes, *see* U.S. Pat. 789422, Feb. 18, 1908.)

To obtain lævulose from sucrose, the latter is first inverted by means of mineral acids or invertase, and the acid removed by neutralisation with baryta or silver oxide. The invert sugar resulting contains both dextrose and lævulose, which may be separated as follows : 6 grams of finely powdered slaked lime is added to every 100 c.c. of a neutral ice-cold 10 p.c. solution of invert sugar, and the solution, which at first sight is merely milky, is agitated, the vessel being preferably immersed in ice-cold water until it acquires a creamy consistency. The mass, which consists of the difficultly soluble calcium lævulosate $CaO \cdot C_6H_{12}O_6 \cdot H_2O$, together with the easily soluble calcium dextrosate, is filtered through linen, and strongly pressed to remove the greater part of the liquid, and is suspended in water and decomposed by addition of oxalic acid or by passage of carbonic acid gas. The filtered solution is evaporated *in vacuô* over sulphuric acid, with production of anhydrous lævulose. Calcium lævulosate dissolves in 137

parts of water at 15°, and is almost insoluble at 0°.

Lævulose, when pure, crystallises from alcohol, and even from aqueous solution, in needles, also in crusts of transparent prisms, which are not hygroscopic. It has m.p. 95°, $D^{17\cdot5}$ 1·669. It sublimes unchanged but very slowly at 100°/1–2 mm. (Ghosh, J. C. S. Abstr. 1917, 112, (i.) 80). It is very soluble in water, almost insoluble in cold absolute alcohol. It is much sweeter than dextrose, and somewhat sweeter than sucrose. It exhibits muta-rotation, and, no doubt, exists in solution as an equilibrated mixture of stereoisomeric γ-oxide forms. The initial rotation $[\alpha]_D^{20}$ −104° falls to $[\alpha]_D^{20}$ −92° (Parkus and Tollens, Annalen, 257. 160). The specific rotatory power is very considerably influenced by changes of temperature and concentration, which cause an alteration in the proportions of the isomerides in the equilibrium mixture. The rotatory power usually taken is $[\alpha]_D^{15}$ −93·8°. It falls 0·6385° for each degree centigrade of increase in temperature, and at 87·3° is equal but opposite to that of dextrose. This property is taken advantage of in determining its proportion in presence of other sugars, the rotation being observed at two different temperatures.

According to Soxhlet, the relative reducing powers of lævulose and dextrose on Fehling's solution, in 1 p.c. solution, are 475 : 513 ; but Allihn finds that if the solutions be boiled for 30 minutes (instead of for 2 minutes, as in Soxhlet's experiments), their reducing powers are identical. On Knapp's mercurial solution their action is the same, but on Sachsse's mercurial solution their actions are 100 (lævulose) and 148·6 respectively.

Oxidation converts lævulose into acids with fewer carbon atoms, glycollic and trihydroxybutyric. On reduction with sodium amalgam, mannitol and sorbitol are formed. Acids attack it far more readily than dextrose with the production of lævulic and formic acids ; alkalis somewhat less readily. Heating concentrated solutions with oxalic acid forms 4-hydroxymethylfurfurol, whilst it interacts with hydrogen bromide in ethereal solution, forming 4-bromomethylfurfurol

CH : C(CH₂Br) | \O (Fenton and Gostling, CH : C(CHO) Chem. Soc. Trans. 1899, 75, 423 ; 1901, 79, 361).

It is fermented by all yeasts which attack dextrose.

By the action of methyl alcohol and hydrogen chloride (0·5 p.c.) at 35°, a syrup is obtained which probably represents a mixture of methyl fructosides. It is partially hydrolysed by yeast extract.

Fructose diacetone $C_{12}H_{20}O_6$, prepared in a similar manner from acetone, forms needles, m.p. 119°–120° $[\alpha]_D$ −161°. An isomeride has m.p. 97° $[\alpha]_D$ −33·7°.

The osazones of lævulose are identical with those of dextrose. Lævulose is more easily oxidised by disubstituted phenylhydrazines, and forms a characteristic osazone with methylphenylhydrazine, long yellow needles, m.p. 158°–160°.

To prepare this, 4 grams of methylphenylhydrazine are added to 1·8 grams lævulose, in 10 c.c. water, and enough alcohol to make a clear solution further 2 c.c. of acetic acid are added, and the mixture heated 5–10 minutes at most on the water-bath. It is then covered and allowed to stand. Within 2 hours red crystals are obtained, which may be recrystallised from 10 p.c. alcohol.

Fructose penta-acetate melts, when pure, at 108°–109°, has $[\alpha]_D$ −121°, and crystallises in brilliant colourless needles, 1 cm. in length (Hudson and Brauns, J. Amer. Chem. Soc. 1915, 37, 1283).
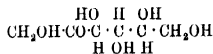
Sorbose (Sorbinose) $C_6H_{12}O_6$ is the keto-hexose obtained from the juice of the mountain-ash berries, which has been exposed to the air and allowed to ferment. The juice contains sorbitol ; this is oxidised by bacterium xylinum to sorbose.

The juices are evaporated to 1·05 sp.gr., allowed to stand some days till the sugar is fermented, and the clear liquid poured into flat dishes and inoculated with an active culture of B.xylinum (Bertrand, Ann. Chim. Phys. 1904, [viii.] 3, 181). Thus is left at 30° till the reduction is a maximum, clarified with lead acetate, excess of lead precipitated as sulphate, and the neutral filtrate concentrated in vacuô. When pure sorbitol is available, 100 grams are dissolved in 500 c.c. water, some nutrient solution for the bacterium added, and the fermentation carried out as above.

Sorbose forms rhombic crystals of a sweet taste, m.p. 154° ; it reduces Fehling's solution, and generally behaves as lævulose, but yields sorbitol on reduction. It is not fermentable by yeasts. It is lævo-rotatory, having $[\alpha]_D$ −42°.

Sorbose phenylosazone is similar to the dextrose compound, but has m.p. 164°.

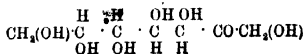The properties are in agreement with the structural formula :

$$\begin{array}{c}\text{HO}\quad\text{H}\quad\text{OH}\\ \text{CH}_2\text{OH·CO·C}\cdot\text{C}\cdot\text{C}\cdot\text{CH}_2\text{OH}\\ \text{H}\quad\text{OH}\quad\text{H}\end{array}$$

Methyl sorbinoside crystallises in transparent thick plates, m.p. 120°–122° (Fischer, Ber. 28, 1159).
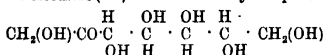
HEPTOSES.

d-Mannoketoheptose. Occurs in the Avocado pear (Persea gratissima) (La Forge, J. Biol. Chem. 1917, 28, 511). It has m.p. 152°, $[\alpha]_D$ +29°. It is not fermented by yeast, and does not show mutarotation. It gives a colour reaction with orcinol and hydrochloric acid like other heptoses. The p-bromophenylhydrazone melts at 179°, the phenylosazone is identical with that from d-mannoaldoheptose.

On reduction the sugar yields d-persitol and d-mannoheptitol.

Since the p-bromophenylhydrazone of d-α-mannoaldoheptose melts at 207°–208°, and that of d-β-mannoaldoheptose is an oil, the configuration of the sugar must be :—

$$\begin{array}{c}\text{H}\quad\text{H}\quad\text{OH OH}\\ \text{CH}_2\text{(OH)·C}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{CO·CH}_2\text{(OH)}\\ \text{OH}\quad\text{OH}\quad\text{H}\quad\text{H}\end{array}$$

Perseulose (*l.c.*) is shown to be l-*galaheptose*:—

$$\text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{C}\quad\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\quad\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\quad\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\quad\overset{\text{H}\cdot}{\underset{\text{OH}}{\text{C}}}\cdot\text{CH}_2(\text{OH})$$

Sedoheptose. Occurs in *Sedum spectabile* (La Forge and Hudson, J. Biol. Chem. 1917, 30, 61) as a non-fermentable, reducing syrup.

Phenylosazone, m.p. 197°; p-*bromophenyl-hydrazone*, m.p. 227°–228°; the *osone* is a syrup, its *o-phenylenediamine derivative* melts at 163°–165°.

Bromine water does not oxidise the sugar, but it reduces with sodium amalgam to two alcohols $C_7H_{16}O_7$:—

·α-Sedoheptitol, m.p. 151°–152°, $[\alpha]_D+2\cdot25°$;

β-Sedoheptitol, m.p. 127°–128°, optically inactive.

The two alcohols are separable by their benzylidene derivatives.

These reactions indicate that the sugar is a ketose.

Anhydrosedoheptose $C_7H_{12}O_6$ is formed when sedoheptose is heated with dilute acids. It forms long white prisms, melting at 155°, $[\alpha]_D-146°$. It shows no mutarotation, does not reduce Fehling's solution, and, when boiled with dilute acid, gives an equilibrium mixture which contains 20 p.c. of sedoheptose.

PENTOSES $C_5H_{10}O_5$.

These are widely distributed in plants, where they are present in the skeletal structure, and do not, like the hexoses, serve as food products. Pentoses also appear to be a constituent of many of the tissues of the animal body, and are sometimes found in urine. Both the natural pentoses, *l*-arabinose and *l*-xylose, belong to the *lævo-* series. Dextrose (*dextro*-glucose), when degraded by the methods of Ruff or Wohl, gives rise to the isomeric *d*-arabinose. However, the natural pentoses are closely related to the natural hexoses. For example, the space arrangement of the groups attached to the upper four carbon atoms is the same in *d*-glucose as it is in *l*-xylose :

CHO	CHO		
HCOH	HCOH	CHO	
HOCH	HOCH	HOCH	
HCOH	HCOH	HCOH	
CH₂OH	HCOH	HCOH	
	CH₂OH	CH₂OH	
l-Xylose,	*d*-Glucose.	*d*-Arabinose.	
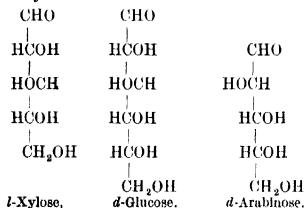
A similar relationship exists between galactose and arabinose, which occur together in many gums, whilst some polysaccharides yield both xylose and glucose on hydrolysis. The pentoses do not occur as such, but in the form of condensation products of high molecular weight, termed 'pentosans' (araban or xylan). These are comparable with the hexose condensation products, starch and cellulose ; as a rule, the pentosans contain both C_5 and C_6 carbohydrates.

The mechanism of the formation of pentoses

in the plant is not yet clear. Some authorities consider they are derived by oxidation from the hexoses ; others advocate the view that they are directly formed in the cell, like the hexoses, but independently of these. Such a transformation as that from dextrose to *l*-xylose has not been effected in the laboratory: the chemical degradation of dextrose by oxidation leads to *d*-arabinose. The pentoses show all the general chemical properties of the hexoses. Biochemically, they are different, being not fermentable by yeasts, whilst their glucosidic derivatives (*e.g.* the methyl arabinosides and xylosides) are not hydrolysed by any of the better-known plant enzymes. They are attacked by a number of bacteria. Characteristic of the pentoses is the formation of furfurol on distillation with hydrochloric acid. They, therefore, show colour reactions with orcinol and phloroglucinol. Equal parts of concentrated hydrochloric acid and water are taken, together with the pentose and a little orcinol or phloroglucinol, and the mixture warmed in the water-bath. With orcinol the solution becomes red, then violet, and finally blue or blue-green, with the separation of a precipitate which dissolves in amyl alcohol, giving a blue-green solution ; this shows an absorption band between C and D. With phloroglucinol the solution becomes cherry-red, and a precipitate is formed, giving a red solution in amyl alcohol, with an absorption band between D and E

l-**Arabinose** $C_5H_{10}O_5$ is obtained by hydrolysis of most gums, particularly gum arabic and cherry gum.

Preparation.—A solution of gum arabic, or allied gum (dextro-rotatory, and yielding little mucic acid by the action of nitric acid, by preference), containing 30–40 grams of the gum, and 2·3 c.c. sulphuric acid in 100 c.c., is boiled for 7–12 minutes, cooled, the acid neutralised with calcium or barium hydroxide or carbonate and alcohol, sp.gr. 0·83 added as long as a precipitate is produced. This precipitate soon settles, leaving the alcoholic solution clear. On distilling off the alcohol and evaporating to a syrup, arabinose crystallises out. The substance is obtained in well-defined rhombic prisms, with monoclinic termination, by recrystallising from water. With some gums the digestion of the acid solution can be continued for 2 hours with increased yield of arabinose, and without impairing the purity of the product. The crystals are anhydrous ; m.p. 160°.

Arabinose has $[\alpha]_D+104°$ to $+105°$, the activity increasing with the strength of the solution, and decreasing as the temperature at which it is observed is raised.

It exhibits muta-rotation, α-arabinose having the initial rotatory power $[\alpha]_D+175°$, decreasing to $+104°$. β-Arabinose has not been isolated. Accordingly, like dextrose, it has a γ-oxidic structure.

The heat of combustion is 558 cals.

Arabinose reduces Fehling's solution, the amounts of copper oxide produced by equivalent weights of arabinose and dextrose being as 111 : 100.

Bromine oxidises it to *l*-arabonic acid $C_5H_{10}O_6$, which crystallises as the lactone $C_5H_8O_5$, m.p. 95°–98°, $[\alpha]_D-73\cdot9°$. Nitric acid

forms oxalic acid as the final product, but in dilute solution, firstly arabonic acid, and secondly *l*-trihydroxyglutaric acid, m.p. 127°, are formed. On reduction, amongst other products, *l*-arabitol, m.p. 102°, is formed, which is optically inactive, but becomes lævo-rotatory in presence of borax.

Arabinose forms an additive compound with hydrogen cyanide, which is hydrolysed to arabinose carboxylic acid. This is, in reality, a mixture of two acids, of which the lactones on reduction give rise to *l*-glucose and *l*-mannose.

The diphenylhydrazone, m.p. 218°, is almost insoluble. The other hydrazones have the following melting-points : phenyl, 151°; *p*-bromophenyl, 150°; α-methylphenyl, 161°; *a*-ethylphenyl, 153°; α-amylphenyl, 120°; α-allylphenyl, 145°; α-benzoylphenyl, 170°; β-naphthyl, 141°. Arabinose phenylosazone, m.p. 160°, is prepared similarly to the dextrose compound. It is slightly more soluble, and, when boiled with benzaldehyde, arabinosone is formed. The *p*-bromophenylosazone has m.p. 196°-200°.

Arabinose forms crystallisable compounds with the aromatic diamines and diamino-acids.

l-Xylose is obtained by the hydrolysis of wood gum (xylan) extracted from wood by dilute soda solution.

According to Bertrand (Bull. Soc. chim. [3] 5, 554), it may be obtained from wheat or oat straw by first extracting the straw with tepid water, and then boiling it for several hours with dilute (1-2 p.c.) sulphuric acid. The liquor, after removal of the sulphuric acid by baryta, is concentrated on the water-bath and treated with alcohol ; this extracts the xylose, which forms a syrup on evaporation of the alcohol, solidifying on the addition of a crystal of xylose. The yield is about 2 p.c. from wheat straw, and 4 p.c. from oat straw.

Another convenient source are oat hulls, which are cleaned by soaking in dilute ammonia, washed and hydrolysed with sulphuric acid. Hudson and Harding (J. Amer. Chem. Soc. 1917, 39, 1038) obtained a yield of 8-12 p.c of xylose by direct acid hydrolysis of cotton-seed hulls. A more suitable source is maize cobs (*idem*. 1918, 40, 1601). Xylose crystallises in orthorhombic prisms, m.p. 144°-145° or 150°-154°. It exhibits muta-rotation, a-xylose having [α]$_D$+79°, falling to +19°, which is the rotation of the equilibrated mixture. The heat of combustion is 561 cals. Bromine oxidises it to xylonic acid, a syrup which is at first lævo-rotatory, but reaches [α]$_D$+17·5°, as it is transformed into the lactone in solution. It forms a very characteristic insoluble compound $C_5H_9O_5CdBr,H_2O$ with cadmium bromide. Nitric acid in the cold forms an optically inactive trihydroxyglutaric acid.

On reduction, inactive xylitol, a syrup, is formed.

α-Methylxyloside has m.p. 90°-92°, [α]$_D$+152; the β-isomeride has m.p. 156°-157°, [α]$_D$-65 9°. With hydrogen cyanide two xylose carboxylic acids are formed, which yield *l*-gulose and *l*-idose on reduction.

The phenylhydrazone has m.p. 116°; the β-naphthylhydrazone, m.p. 70°; and the phenyl-osazone, m.p. 166°.

The methyl pentoses are pentose carbohydrates, in which one of the hydrogen atoms in the primary alcohol group is replaced by methyl. They appear to be widely distributed, but their biochemical significance is not yet understood. They show the same reactions as the pentoses, and, like these, are not fermented by yeasts. Characteristic is the formation of methylfurfur-aldehyde on distillation with acids.

Rhamnose (*Isodulcitol*) $C_6H_{12}O_5,H_2O$, on account of its empirical formula, and the ease with which it crystallised, was formerly classed with dulcitol and mannitol, hence the original name of *iso*dulcitol. Its chemical behaviour shows it to be a methyl pentose. It appears to be widely distributed in nature in the form of glucosides, the best known of which are xanthorhamnin, the colouring matter of Persian berries and quercitrin. Other glucosides containing rhamnose are baptisin, fisetin, frangulin, fustin, datiscin, glycyphyllin, hesperidin, naringin, rutin, sophorin (*v.* GLUCOSIDES).

It is prepared by extracting Persian berries with hot alcohol, distilling off the alcohol, and heating the xanthorhamnin on the water-bath for 2 hours, with 6 p.c. sulphuric acid. The precipitated rhamnetin is filtered, the filtrate neutralised with barium carbonate, and, after removal of the barium sulphate, evaporated to a syrup. This is diluted hot with absolute alcohol, and the solution allowed to stand, when it deposits hard lustrous crystals of rhamnose. About 15-20 grams are obtained per kilo. of berries.

It is advantageously prepared from the residues of the manufacture of quercitron extract, when these are available.

Rhamnose has the constitutional formula :
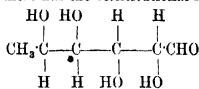
Until recently the positions of the groups attached to the carbon atom next to the CH_3-group were uncertain, but Fischer and Zach (Ber. 1912, 45, 3761) have obtained *d*-isorham-nose by a series of reactions from triacetyl dibromoglucose, in which compound the two halogen atoms are attached to the terminal carbon atoms of the sugar chain.

The hydrate softens at 89°; m.p. 92°-93.° When anhydrous, it crystallises from acetone in needles ; m.p. 122°-126° (Fischer), 108° (Tanret). Like dextrose, it exists in α- and β- modifications, which are in equilibrium in solution. The α-form has [α]$_D$-17°; the β- form [α]$_D$+31·5°; and the equilibrated mixture has [α]$_D$+9°. It sublimes slowly and unchanged at 105°/1-2 mm.

Bromine oxidises it to rhamnonic acid ; with nitric acid it yields a mixture of formic, oxalic, and trihydroxyglutaric acids $C_5H_8O_7$. On reduction, the corresponding alcohol rhamnitol is formed.

The phenylhydrazone has m.p. 159°; methyl-phenylhydrazone, m.p. 124°; ethylphenyl-hydrazone, m.p. 124°; allylphenylhydrazone, m.p. 135°; amylphenylhydrazone, m.p. 99°; diphenylhydrazone, m.p. 134°; benzylphenyl-hydrazone, m.p. 121°; β-naphthylhydrazone, m.p. 170°. Rhamnose phenylosazone crystal-lises in slender yellow needles, slightly soluble in boiling water ; m.p. 190°-192°.

Methylrhamnoside has m.p. 108°-109°, $[a]_D -62^5$; acetone rhamnoside, m.p. 90°-91°.

Other derivatives are rhamnose ethylmercaptal, m.p. 135°-137°; rhamnose oxime, m.p. 127°-128°; rhamnose anilide, m.p. 118°.

Fucose $C_6H_{12}O_5$

$$CH_3 \cdot CH(OH) \overset{H}{\underset{OH}{-}} \overset{H}{\underset{OH}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot CHO$$
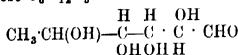
is obtained by hydrolysing the polymer fucosan, which is a component of the cell-wall of many marine algæ. It is also present in *Fucus vesiculosus*, in laminaria and Carragheen moss. The seaweed is washed with water and dilute hydrochloric acid, and boiled for 12 hours with 3 p.c. sulphuric acid. The acid is neutralised with baryta, the filtrate concentrated to a syrup, taken up with alcohol, concentrated again, and the sugar isolated as hydrazone. Reduction with sodium amalgam gives *d*-fucitol (Votoček, 1913, 46, 3653), m.p. 153°-154°, which combines with rhoditol to form *r*-fucitol.

Fucose crystallises slowly in minute needles, m.p. 130°-140°. It exhibits muta-rotation $[a]_D$, being initially $-112°$, falling to $-74.4°$ to $-77°$.

The phenylhydrazone has m.p. 170°-172°; the phenylmethylhydrazone, m.p. 177°; phenylbenzylhydrazone, m.p. 172°-173°; diphenylhydrazone, m.p. 198°; *p*-bromophenylhydrazone, m.p. 181°-184°. Fuconic acid lactone has m.p. 106°-107°, $[a]_D +73°$ to $+78.3°$.

Epifucose. Fuconic acid lactone, heated with pyridine at 145°-150°, is converted to epifuconic acid lactone (Votoček and Červený, Ber. 1915, 48, 658), which on reduction with sodium amalgam gives *epifucose*.

$$CH_3 \cdot CH(OH) \cdot \overset{H}{\underset{OH}{C}} \cdot \overset{H}{\underset{OH}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot CHO$$
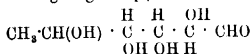
a syrup, $[a]_D -9°$, whose phenylhydrazone and *p*-bromophenylhydrazone are identical with those of fucose.

Rhodeose is the optical antipode of fucose (Müther and Tollens, Ber. 1904, 37, 306). It has $[a]_D +73°$ to $+75.2°$, and forms derivatives having the same melting-point as those from fucose just described. Rhodeonic acid lactone has m.p. 105.5°, $[a]_D -76.3°$ to $-69.4°$. Rhodeose is obtained from the glucoside convolvulin.

The configuration of rhodeose is shown by the following reactions (Hudson, J. Amer. Chem. Soc. 1911, 33, 405; Votoček, Ber. 1910, 43, 476):—

(*a*) Oxidation of rhodeonic acid lactone gives *l*-trioxyglutaric acid.

(*b*) Reduction of rhodeose gives rhoditol, not attacked by sorbose bacterium.

(*c*) The rhodeohexonic acid produced by applying the cyanohydrin reaction to rhodeose yields, on oxidation, saccharic acid.
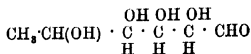
Hence rhodeose is

$$CH_3 \cdot CH(OH) \cdot \overset{OH}{\underset{H}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot \overset{H}{\underset{OH}{C}} \cdot CHO$$
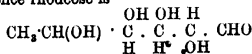
Epirhodeose (Votoček, Ber. 1911, 44, 362). Rhodeonic acid, heated with pyridine at

150°-160°, is epimerised to epirhodeonic acid, the lactone of which on reduction gives *epirhodeose*:

$$CH_3 \cdot CH(OH) \cdot \overset{OH}{\underset{H}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot CHO$$

The sugar is a syrup which gives the same osazone as rhodeose; it oxidises to trioxyribo-glutaric acid, m.p. 184°-185°, $[a]_D +12°$.

Isorhodeose (Votoček, Ber. 1910, 43, 476; 1911, 44, 819, 3287).

This occurs combined with rhodeose, rhamnose, and other compounds in the glucoside convolvulin; it is the optical antipode of Fischer's *isorhamnose*. The configuration is shown by the following reactions:—
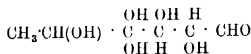
(*a*) Oxidation with nitric acid produces *i*-trioxyglutaric acid.

(*b*) Oxidation with bromine water gives isorhodeonic acid, which reacts:—

(i) With pyridine at 150° to give antirhamnonic acid, which reduces to *antirhamnose*. HCN converts this sugar to anti-rhamnohexonic acid, which may be further oxidised, giving *mucic acid*.

(ii) With H_2O_2 in presence of iron to give a methyltetrose, which oxidises to *l*-tartaric acid.

Isorhodeose is therefore

$$CH_3 \cdot CH(OH) \cdot \overset{OH}{\underset{OH}{C}} \cdot \overset{OH}{\underset{H}{C}} \cdot \overset{H}{\underset{OH}{C}} \cdot CHO$$

it has $[a]_D +31.5°$, and the melting-points of the phenylosazone and *p*-bromophenylosazone are respectively 186°-187° and 222°.

TETROSES.

By reduction of dioxyvalerolactone, a mixture of a methyltetrose and the corresponding alcohol were produced. The *methyltetrose* is a syrup, giving an *osazone*, m.p. 140°-142°, and a *phenylbenzylhydrazone*, m.p. 99°-100°. The *methyltetritol* is also a syrup, its *tetrabenzoate* melting at 136°-137° (Gilmour, Chem. Soc. Trans. 1914, 105, 73).

Rhodeotetrose. Rhodeose is degraded by Wohl's method to a *rhodeotetrose*, the *p*-bromophenylhydrazone of which melts at 143°-144° (Votoček, Ber. 1917, 50, 35).

Chinovose $C_6H_{12}O_5$ is only known as a constituent of the glucoside chinovin, which, on hydrolysis with alcoholic hydrochloric acid, yields ethylchinovoside $C_6H_{11}O_4 \cdot OC_2H_5$, originally termed chinovite, $[a]_D +78°$.

Chinovite, when hydrolysed with dilute sulphuric acid, yields chinovose, which is a syrup, showing all the reactions of the carbohydrates. Phenylchinovosazone forms yellow needles; m.p. 193°-194°.

Apiose $C_5H_{10}O_5$ is an altogether remarkable sugar, obtained together with dextrose on hydrolysing the glucoside apiin present in the seeds and leaves of parsley. It contains a branched chain of carbon atoms, having the constitutional formula

$$\begin{matrix} CH_2(OH) \\ CH_2(OH) \end{matrix} > CH(OH) \cdot CH(OH) \cdot CHO$$
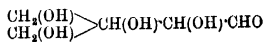
(Vongerichten, Annalen, 1901, 318, 121; 1902, 321, 71; Ber. 1906, 39, 235).

It is a pale yellow syrup, optically inactive,

non-fermentable, does not yield furfurol, and yields isovaleric acid when reduced by hydrogen iodide and phosphorus. Bromine oxidises it to apionic acid.

The phenylhydrazone has m.p. 135°; phenylosazone, m.p. 156°; and the bromophenylosazone, m.p. 209°–212°.

Digitoxose $C_6H_{12}O_4$ is obtained on hydrolysing digitoxin, one of the glucosides of digitalis. It crystallises in prisms or plates, m.p. 102°, and is dextro-rotatory. It has the composition (Kiliani) $CH_3 \cdot CH(OH) \cdot [CH(OH)]_2 \cdot CH_2 \cdot CHO$.

Digitalose $C_7H_{14}O_5$ is similarly obtained from digitalin.

THE CARBOHYDRATE ACIDS

are those containing the same number of carbon atoms as the aldose carbohydrates from which they are derived. They are either mono- or dibasic. Ketoses yield acids with fewer carbon atoms than the original carbohydrate on oxidation.

The monobasic acids are formed on oxidising the aldehyde group to acid, generally by means of bromine or dilute nitric acid. More energetic oxidation converts also the primary alcohol $(-CH_2 \cdot OH)$ group into acid (CO_2H).

Glucuronic acid, which is of importance physiologically, is a type of monobasic acid, in which the aldehyde group is intact, and the primary alcohol group oxidised to acid. The monobasic acids are transformed in aqueous solution, particularly on evaporation on the water-bath, into lactones which crystallise well. The dibasic acids similarly sometimes form double lactones.

The most important property of gluconic and isomeric acids is their behaviour on heating with pyridine or quinoline, when they are transformed into isomerides, rearrangements of the groups attached to the α-carbon atom taking place. Thus, when gluconic acid is heated with quinoline or pyridine at 130°–150°, it is partially converted into mannonic acid. This behaviour has been of the utmost importance in effecting the synthesis of the carbohydrates.

Gluconic acid $C_6H_{12}O_7$ always contains a proportion of lactone. It is slightly lævo-rotatory at the instant of solution, but becomes dextro-rotatory as the transformation to lactone takes place, the final figure for a mixture in equilibrium of acid and lactone being about $+19°$. The lactone crystallises in slender needles, m.p. 130°–135°. It has [a] $+68°$ when first dissolved, falling to $+19°$ for the solution in equilibrium with the acid. The calcium salt is sparingly soluble and characteristic, likewise the phenylhydrazide $C_6H_{12}O_6 \cdot N_2H_2Ph$, which forms colourless prisms, m.p. 200°.

Mannonic acid. The lactone crystallises in needles, m.p. 149°–153°, [a]$_D$ $+53 \cdot 8°$. The phenyl hydrazide has m.p. 214°–216°.

Galactonic acid is obtained by oxidising galactose or hydrolysed lactose with bromine. In the latter case, 100 grams lactose are boiled 4 hours with 400 grams 5 p.c. sulphuric acid, the acid precipitated as barium sulphate, and the filtrate evaporated to 300 c.c., cooled to 35°, and 200 grams of bromine added with constant shaking. After standing for a short time, the excess of bromine is removed by a current of air, hydrogen bromide by lead carbonate and silver oxide, and the solution is saturated with cadmium

carbonate, and concentrated till the cadmium galactonate crystallises. The mother liquors yield a second crop, about 50 grams in all being obtained. This salt is purified and decomposed with sulphuric acid.

Galactonic acid crystallises in needles, which, on heating to 100°, lose water, forming the lactone. The lactone crystallises with difficulty; it has m.p. 90°–92°, and forms a crystalline hydrate, m.p. 65°. The acid has [a]$_D$ $-10 \cdot 5°$, which becomes $-57°$ on heating. The lactone has [a]$_D$ $-70°$, and the crystalline hydrate [a]$_D$ $-58°$. The cadmium salt is characteristic; the phenylhydrazide has m.p. 200°–205°. On heating with pyridine at 150°, galaptonic acid is partially converted into d-talonic acid.

Lactobionic and maltobionic acids, obtained by the action of bromine on the corresponding disaccharides, are colourless syrups or amorphous compounds.

Glucuronic acid (glycuronic acid) $C_6H_{10}O_7$ is frequently found in urine, combined with a variety of substances, forming compounds of a glucosidic nature. It was synthesised by Fischer (Ber. 24, 521), by reduction of saccharic acid lactone, and has the formula

$$CO_2H \cdot [CH \cdot OH]_4 \cdot CHO$$
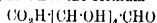
It is conveniently prepared from euxanthic acid, which is readily hydrolysed by dilute acids to glucuronic acid and euxanthon

$$C_{10}H_{16}O_{10} + H_2O = C_6H_{10}O_7 + C_{13}H_8O_4$$
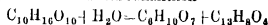
Euxanthic acid, known in commerce as Indian yellow or piuri, is a pigment made almost exclusively in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves (e. INDIAN YELLOW).

According to Thierfelder (Zeitsch. physiol. Chem, 11, 388), 1 part of euxanthic acid is heated with 200 parts of water in an autoclave at 120°, the euxanthone separated by filtration, and the solution concentrated. Owing to the introduction of aniline dyes, piuri has become very rare and expensive.

Neuberg and Lachmann (Biochem. Zeitsch. 1910, 24, 416) propose to obtain glucuronic acid by feeding menthol to rabbits. Menthol has the advantage that it is not poisonous, the paired glucuronic acid is fairly easily isolated and readily hydrolysed. 2 grams menthol are dissolved in 1 c.c. alcohol and shaken with 20 c.c. lukewarm water; this emulsion is administered to rabbits, and the urine collected, rendered acid, and extracted with ether. Excess of ammonia is added to the ethereal solution, and the ether distilled off. The residue of insoluble ammonium menthylglucuronate is dissolved in water, precipitated by lead acetate, the precipitate decomposed with hydrogen sulphide, and the filtrate evaporated, when pure menthylglucuronic acid is obtained. This is decomposed by boiling with dilute sulphuric acid to give glucuronic acid.

Glucuronic acid is a syrup, and is transformed into the crystalline lactone on evaporation. This is very soluble in water; it has m.p. 175°, [a]$_D$ $+19°$. It reduces Fehling's solution, yields furfurol on distillation with mineral acids, showing positive reactions with orcinol and phloroglucinol, and is not fermentable.

A number of substances when introduced

into the animal body are excreted in the urine as lævo-rotatory-paired glucuronic acid derivatives. These are isolated by precipitation with basic lead acetate, of which an excess should be avoided.

Saccharic acid $C_6H_{10}O_3$

$$CO_2H—C—C—C—C—CO_2H$$
$$\begin{array}{c} OH\ H\ OH\ OH \\ \\ H\ \ OH\ H\ \ H \end{array}$$
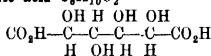
is obtained on oxidising dextrose and all carbohydrates which contain dextrose, also from sorbitol, gluconic acid and glucuronic acid. It is prepared from starch or dextrose (50 grams) by heating with nitric acid (350 grams) (sp.gr. 1·15) on the water-bath, and evaporating to a syrup whilst stirring continually. A little water is added, and the solution again evaporated. The residue is dissolved in 150 grams of water, neutralised with a concentrated solution of potassium carbonate, 25 c.c. acetic acid (50 p.c.) added, and the solution evaporated to 80 c.c. On standing, the monopotassium salt separates, and is recrystallised from a little hot water. In the mother liquors, Neuberg (Biochem. Zeitsch. 1910, 28, 355) has recently found 10 p.c. of an acid identical or isomeric with glucuronic acid.

Saccharic acid is a syrup, $[\alpha]_D + 8°$, increasing to $+22·5°$. The lactone $C_6H_8O_7$ has m.p. 130°–131°, $[\alpha]_D + 37·9°$, decreasing to 2·25° for the equilibrium mixture with the acid. Characteristic is the monopotassium salt $C_6H_9O_8K$, formed on the addition of acetic acid in excess to a solution of the normal saccharate. This crystallises in small orthorhombic needles, sparingly soluble in water (1·12 parts per 100°). The diphenylhydrazide has m.p. 210°.

The continued action of nitric acid forms tartaric and racemic acids, and, finally, oxalic acid. On dry distillation it decomposes with the evolution of carbon dioxide, yielding pyromucic and *iso*pyromucic acids.

Mucic acid $C_6H_{10}O_8$

$$CO_2H—C—C—C—C—CO_2H$$
$$\begin{array}{c} OH\ H\ \ H\ \ OH \\ \\ H\ \ OH\ OH\ H \end{array}$$
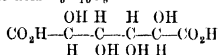
is obtained on oxidising galactose, lactose, raffinose, dulcitol, and all carbohydrates which yield galactose when hydrolysed.

100 grams of lactose are heated on the water-bath with 1200 c.c. of nitric acid sp.gr. 1·15 till the volume is reduced to 200 c.c.; this residue is taken up with an equal volume of water and left to crystallise; the yield is about 38 grams.

Mucic acid is a microcrystalline powder, m.p. 213°–214°; it dissolves in 300 parts of water at 14°, or 60 parts at 100°. It is optically inactive, and cannot be resolved into optically active isomerides.

It forms normal and acid salts with metals, and normal salts with alkaloids. The mono-phenylhydrazide has m.p. 190°–195°; the diphenylhydrazide, prepared by heating with phenylhydrazine acetate on the water-bath, has m.p. 240°.

THE CARBOHYDRATE ALCOHOLS

are widely distributed in the vegetable kingdom, where they occur, as a rule, uncombined with other substances. As a class they are readily soluble in water, crystallise well, and have a small

rotatory power. On cautious oxidation they give in turn a reducing sugar, monobasic acid, and dibasic acid. They are obtained by reduction of the corresponding aldose or ketose carbohydrates with sodium amalgam, but, as a rule, owing to transformations in the alkaline solution, a mixture of alcohols is produced. They are not fermentable, and do not reduce Fehling's solution. Only those which occur naturally will be described here, though the alcohols corresponding to the synthetical sugars are known.

Erythritol $C_4H_{10}O_4$

$$CH_2(OH)—C—C—CH_2(OH)$$
$$\begin{array}{c} OH\ OH \\ \\ H\ \ H \end{array}$$
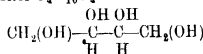
occurs in a number of lichens, particularly the varieties of *Roccella tinctoria*, where it is present in the form of the ether erythrin $C_{20}H_{22}O_{10}$, which is a diorsellinate of erythritol. This is saponified by boiling with baryta or lime

$$C_{20}H_{22}O_{10} + 2H_2O = C_4H_{10}O_4 + 2C_7H_8O_2 + 2CO_2$$

Erythrin is heated for about 2 hours at 150° in a closed iron vessel, with a quantity of milk of lime somewhat less than sufficient to decompose it; the exclusion of air prevents the formation of a large quantity of resinous matter. The liquid filtered from calcium carbonate, on evaporation at a gentle heat, deposits orcinol in fine crystals, and the mother liquors on further evaporation yield a crystalline mass of orcinol and erythritol, from which the former is extracted by ether (v. De Luynes, Compt. rend. 56, 803). Stenhouse (Chem. Soc. Trans. [2] 5, 222) dissolves the erythrin in a slight excess of milk of lime, boils for half an hour in a vessel with a long condensing tube to exclude air, precipitates the lime in the resulting solution with carbon dioxide, or (on a large scale) by exact neutralisation with dilute sulphuric acid, and evaporates the filtered solution to dryness. On digesting the residue for 20–30 minutes with a mixture of benzene, toluene, &c. (b.p. 110°–150°), in a metallic vessel provided with a condenser, an undissolved portion is left free from orcinol, which, on evaporation and filtering from resin, &c., deposits crystals of erythritol. These may be purified by washing with cold alcohol, pressing, and recrystallising once or twice from hot water.

Erythritol crystallises in large, colourless, transparent quadratic prisms, having an adamantine lustre. Sp.gr. 1·542–1·449. It melts at 126° (Liebermann, Ber. 17, 873), and may be cooled far below its melting-point without solidifying.

It is optically inactive even in presence of borax, and has no action on litmus, but the addition of borax renders it acid. Its taste is sweet, but less so than that of orcinol. It is very readily soluble in water, its heat of solution being at 18°, 5·2 cals., and at 9°, 5·12 cals. (Colson, Compt. rend. 104, 113), sparingly in cold alcohol and insoluble in ether. It does not lose water below 100°, and does not precipitate neutral or basic lead acetate, copper salts, or ammonium lead nitrate (Stenhouse).

Erythritol is not altered by ammonia, by bromine, or by chloride of lime. Heated to 260° with solid potassium hydroxide, it yields oxalic and acetic acids with evolution of hydrogen. With fuming hydriodic acid, it gives secondary butyl iodide $C_4H_9·HI$. It is attacked by atmospheric oxygen in presence of platinum

black, forming trihydroxybutyric and oxalic acids (De Luynes, Compt. rend. **56**, 803 ; Sell, *ibid.* **61**, 741).

With dilute nitric acid, oxalic acid, tartaric acid, and a large quantity of hydrocyanic acid are produced ; and with chromic acid and potassium permanganate, or with chromic mixture, formic acid, carbon dioxide, and oxalic acid are obtained (Przybytek, Bull. Soc. chim. [2] **35**, 108).

E. Fischer and J. Tafel (Ber. **20**, 1088), by the oxidation of erythritol with dilute nitric acid, procured a reducing sugar, erythrose, formed a crystalline phenylosazone $C_{16}H_{18}N_4O_2$, m.p. 166°-167°, sparingly soluble in water, more readily in ether and benzene. The tetranitrate $C_4H_6(NO_3)_4$ forms large shining laminæ, m p 61°.

When erythritol is dissolved in concentrated sulphuric acid, and the mixture heated to 60°-70°, the compound $C_8H_{11}O_2(SO_4H)_3$ is produced, which forms salts with metals (Hesse, Annalen, 117, 329).

Erythritol dissolves easily in chlorosulphonic acid, forming erythritol tetrasulphuric acid $C_4H_6(SO_4H)_4$, which crystallises in snow-white masses consisting of small prisms It is decomposed by hot water with regeneration of erythritol. The metallic salts are sparingly soluble.

By heating erythritol for about 100 hours with 12–15 parts concentrated hydrochloric acid, De Luynes (Ann Chim. Phys. [4] 2385 ; J. 1864, 497) obtained erythritol dichlorohydrin $C_4H_6(OH)_2Cl_2$. By raising the temperature to 120°-130°, the result is more quickly attained, or the compound may be produced by heating erythritol to 120°-130° in a current of hydrochloric acid (Przybytek, Ber. **14**, 2072). It melts at 124° 125° (m.p. 145°, De Luynes).

Erythritol tetrachloride $C_4H_6Cl_4$, produced by the action of phosphorus pentachloride, melts at 73°, and crystallises in prisms (Henninger, Bull. Soc. chim. **34**, 194 ; Bell, Ber **12**, 1271). Dinitrodichlorhydrin $C_4H_6(Cl_2)(NO_2)_2O_2$, has m.p 60°. Erythritol dibromhydrin $C_4H_6(Br_2)(OH)_2$ is formed by heating with a saturated solution of hydrobromic acid for 3 hours at 100° in a sealed tube. It is insoluble in water, and melts at 130° (Champion, Compt. rend. **73**, 114). Dinitrodibromhydrin $C_4H_4(Br_2)(NO_2)O_2$ is a flaky precipitate, m.p. 75°. It does not detonate under the hammer (Champion).

The tetraformate forms long slender needles, m p. 150° ; the tetracetate has m.p. 85° ; and the tetrabenzoate, m.p. 186°-187°.

Characteristic is the dibenzylideneacetal $C_4H_6O_4(C_7H_6)_2$, obtained on shaking with 2 parts of benzaldehyde and 3 parts of 50 p.c. sulphuric acid (Fischer, Ber. **27**, 1524) which forms slender needles sparingly soluble in hot water.

It is not fermentable by yeasts. *Bacterium xylinum* transforms it into a reducing ketotetrose (Bertrand, Compt. rend. **126**, 762), and it is attacked by bacteria in cow-dung and hay water, succinic acid in the one case and volatile acids in the other being the main products of change (Fitz, Ber. 11. 1890 ; **12**, 474).

The anhydride αδ-oxy-βγ-butanediol is obtained by heating erythritol for some hours with acids ; it is a liquid, b.p. 154°-155° at 18 mm.

The second anhydride $C_4H_6O_2$ was prepared by Przybytek (Ber. 17, 1091) by the action of potash on erythritol dichlorhydrin. It is a colourless mobile volatile liquid, b.p. 138°, sp.gr.

1·1322. It combines with water, acids, and ammonia, and forms compounds with hydrocyanic acid and aniline. Its constitutional formula is

$$CH_3 \cdot CH \cdot CH \cdot CH_3$$
$$\diagdown O \diagup \quad \diagdown O \diagup$$
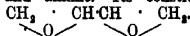
When heated with anhydrous barium oxide for 3 days at 200°-220°, the anhydride yields furfurane ; when heated with phosphorus pentasulphide it gives thiophene.

Adonitol $C_5H_{12}O_5$

$$OH \; OH \; OH$$
$$CH_2(OH) - C - C - C - CH_2(OH)$$
$$H \quad H \quad H$$
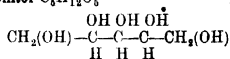
is the only naturally occurring pentose alcohol ; it corresponds to ribose, and is obtained on reducing this. It is found in *Adonis vernalis* (Podwyssotzki, Arch. Pharm. 1889, 141). It separates from water in transparent prismatic crystals m p. 102°. It has a sweet taste, and is optically inactive. When shaken with benzaldehyde and 50 p.c. sulphuric acid, the dibenzylidene acetal is formed quantitatively ; it crystallises in slender needles, m.p. 164°-165°. The corresponding diformylideneacetal has m.p. 145°. It is oxidised to a mixture of pentoses (Fischer, Ber. 1893, 26, 633 ; 27, 2491 ; Merck, Arch. Pharm. 1893, 231, 129).

Mannitol or *d*-**mannite** $C_6H_8(OH)_6$

$$H \quad H \quad H$$
$$CH_2OH - C - C - C - C - CH_2OH$$
$$OH \; OH \; H \quad H$$
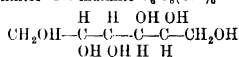
is the alcohol corresponding to mannose. It was first found in the dried exudation from the manna ash, *Fraxinus ornus*, by Proust, in 1806, and is widely distributed in plants. It is contained in the sap of the larch, in monkshood, in the leaves of *Syringa vulgaris*, in celery, sugar cane, in fungi, where it exceeds dextrose in quantity or even replaces it. Thus *Lactarius pallidus*, when dried, contains from 10 to 15 p.c. (Bourquelot, Compt. rend. 108, 568), and *Agaricus integer* is also a good source. Kylin (Zeitsch. physiol. Chem. 1913, 83, 171) has found it in several *Fucus* and *Laminaria* species. It also occurs in the sap of French beans on keeping. It is prepared from manna by extraction with boiling alcohol. Mannitol is obtained on reducing mannose, lævulose, or dextrose with sodium amalgam. In many cases it seems to be a fermentation product derived from trehalose (Busolt, Chem. Soc. Abstr. 1913, i. 803). Its formation may be avoided by preserving plant extracts under sterilised conditions.

It crystallises in colourless rhombic prisms, m.p. 166°. 100 parts of water dissolve 16 parts at 16°, 100 parts of alcohol dissolve 0·07 part at 14°. It is optically inactive, but on the addition of borax it becomes strongly dextro-rotatory, a mixture containing 10 p.c. mannitol and 8 p.c. borax having $[\alpha]_D + 22·5°$. This mixture is strongly acid. With caustic soda and other alkalis it becomes lævo-rotatory.

Mannitol has a slightly sweet taste, is not fermentable by yeast, sorbose bacteria oxidise it to lævulose, and it is attacked by many other races. It does not reduce Fehling's solution, or interact with phenylhydrazine.

Mannitol is easily oxidised. Air in presence of platinum black forms mannosaccharic acid,

and a mixture of mannose and lævulose, which is also formed with hydrogen peroxide and an iron salt. Bromine gives mainly lævulose. Nitric acid transforms it into mannosaccharic acid and finally into glycollic acid and oxalic acids.

Derivatives.—On heating at 280°, mannitol is converted by loss of water into mannitan $C_6H_{12}O_5$, which is formed at 100° in presence of strong acids. The hexanitrate, also known as nitromannitol $C_6H_8(NO_3)_6$, is prepared by the action of a mixture of sulphuric and nitric acids ; it forms colourless acicular crystals, m.p. 112°–113°, $[\alpha]_D + 40°$, which explode violently on being struck or when suddenly heated.

The dichlorohydrin has m.p. 174°, $[\alpha]_D - 3.75°$; and its tetranitrate forms slender needles, m.p. 145°. The hexacetate (Franchimont, Ber. 12, 2059) separates from alcohol in orthorhombic crystals, m.p. 119°–120°, $[\alpha]_D + 18°$. The hexabenzoate has m.p. 149°.

The tribenzylidene acetal crystallises in slender needles, insoluble in water ; m p. 218°–222° (Fischer, Ber. 28, 1975). Triacetone mannitol (Fischer, *ibid.* 28, 1167) forms colourless prisms, m.p. 68°–70°, $[\alpha]_D + 12.5°$. It tastes bitter. Mannitol monoacetone, treated with benzoyl chloride and quinoline at 15° for five days, yields tetrabenzoylmannitol monoacetone, m.p. 122°–123°, which hydrolyses partially to tetrabenzoylmannitol, m.p. 122°–123°, $[\alpha]_D + 8°$. (E. Fischer, Ber. 1915, 48, 266.)

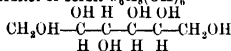For the conversion of mannitol into methyl-a-pyren

$$\begin{array}{c} CH \\ HC \diagdown CH \\ \| \quad \| \\ HC \quad CHMe \\ \diagdown O \diagup \end{array}$$
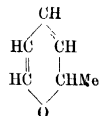
see Windaus and Tomiclŕ (Chem. Zentr. 1918, ii. 109).

The anhydride mannitan exists in amorphous and crystalline modifications, the latter having m.p. 137°, $[\alpha]_D - 24°$. A second anhydride is mannide $C_6H_{10}O_4$, which exists in several forms. One obtained by reducing the dichlorohydrin crystallises in slender needles or large prisms, m.p. 119°, $[\alpha]_D + 94°$; *iso*-mannide produced by the dry distillation of mannitol *in vacuó*, forms prisms, m.p. 87°, $[\alpha]_D + 91.4°$.

d-**Sorbitol** or sorbit $C_6H_8(OH)_6$

$$\begin{array}{c} OH \ H \quad OH \ OH \\ | \quad | \quad \quad | \quad | \\ CH_2OH-C-C-C-C-CH_2OH \\ | \quad | \quad \quad | \quad | \\ H \ OH \ H \ H \end{array}$$

is the alcohol corresponding to dextrose, from which it is obtained on reduction with sodium amalgam in faintly alkaline solution. Sorbitol was discovered in mountain-ash berries by Boussingault (Compt. rend. 1872, 74, 939), and occurs in the fruits of a large number of plants belonging to the *Rosaceæ*. It was found as a crystalline network on the dried heads of the fungus *Boletus bovinus* (von Lippmann, Ber. 1912, 45, 3431).

It is prepared from the expressed juice of mountain-ash berries, which is fermented to remove carbohydrate, defecated with basic lead acetate, and concentrated to a syrup *in vacuó*.

This syrup is taken up with alcohol, and usually gives crystals of sorbitol. In other cases an equal weight of 50 p.c. sulphuric acid, and a little less benzaldehyde is added, and the mixture agitated. After 24 hours it sets to a crystalline mass of dibenzylidene sorbitol. This is separated, washed, and decomposed by boiling with dilute sulphuric acid.
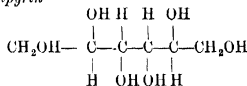
The benzaldehyde is removed by steam distillation, sulphuric acid by baryta, and the benzoic acid extracted by ether. The liquid is concentrated to a syrup, and inoculated with a crystal of sorbitol (Vincent and Delachanal, Compt. rend. 108, 147). This method permits of the separation of sorbitol in small quantities from plants.

Sorbitol crystallises with 1 mol. H_2O in slender needles, m.p. 55°. The anhydride has m.p. 110°. It is very soluble in water, sparingly so in alcohol. It has $[\alpha]_D - 17.3°$, which becomes $+1.4°$ in presence of borax. It is faintly sweet, non-fermentable, but is oxidised by *B-xylinum* to sorbose (*q.v*).

The hexacetate has m.p. 99°. The dibenzylidene acetal as obtained above is a mixture of two isomerides, one of which has m.p. 163°–164°. Triacetone sorbitol has m.p. 45°.

Styracitol, a naturally occurring substance isolated by Asahina (Ber 1912, 45, 2363) from *Styrax abassia*, is isomeric with the anhydrosorbitol obtained by reduction and hydrolysis of anhydromethylglucoside (Fischer and Zachs Ber. 1912, 45, 456, 2068). This suggests that such anhydrides of glucose and of glucoside occur in nature.

Dulcitol. *Dulcin, Dulcose, Melampyrite, Melampyrin*

$$\begin{array}{c} OH \ H \quad H \ OH \\ | \quad | \quad \quad | \quad | \\ CH_2OH- C-C-C-C-CH_2OH \\ | \quad | \quad \quad | \quad | \\ H \quad OH \ OH \ H \end{array}$$

is the alcohol corresponding to galactose.

Occurrence.—Found in a manna or crude preparation from a bulbous root of unknown origin from Madagascar (Laurent, Annalen, 76, 358; Jacquelain, *ibid.* 80, 345, in *Scrophularia nodosa* and *Rhinanthus Crista galli* (Eichler, Ueb. d. Melampyrin, Moscow, 1885) ; in *Melampyrum nemorosum* (Hünefeld, J. pr. Chem. 4, 233 ; Gilmer, Annalen, 123, 372) ; in *Euonymus europæa* (Kubel, P. Pharm. Chim. 85, 372), and in dulcite manna (Hecht, Annalen, 165, 148).

Preparation.—Dulcitol is prepared from the Madagascar material by extracting with boiling water and allowing the filtrate to crystallise. To prepare it from the plants above-mentioned, they are gathered at a suitable time and dried. A decoction is made of them, rendered alkaline with milk of lime, boiled, filtered, concentrated, and acidified with hydrochloric acid. Dulcitol crystallises out on cooling. *Dulcite manna* is extracted with boiling alcohol ; dulcitol crystallises from the solution filtered hot. The manna yields 72 p.c. dulcitol (Hecht).

Dulcitol may also be prepared by the reduction of galactose with sodium amalgam, the soda produced being from time to time neutralised with sulphuric acid. It is obtained mixed with mannitol on reducing lactose.

Properties.—Dulcitol, both of natural and synthetical origin, crystallises in colourless, highly lustrous monoclinic prisms with octahedral summits. The crystals are gritty between the teeth, and taste very faintly sweet; m.p. 118°. One part dulcitol dissolves in 34·41 parts water at 16·5°; it is but slightly soluble in alcohol, even at a boiling temperature. It is optically inactive, even in presence of borax; the derivatives are also inactive. Its solutions are not coloured brown by potash, nor do they reduce alkaline copper solutions. Nitric acid oxidises it to mucic acid; oxalic and racemic acids are also produced (Carlet, Compt. rend. 51, 137; 53, 343). Yeasts do not ferment it, but other organisms, such as exist in cheese, convert it, in presence of calcium carbonate, into alcohol, lactic, and butyric acids. A saturated solution containing dulcitol and borax in the proportion of 2 mols. dulcitol to 1 mol. borax is neutral, but if the proportion of borax is less, the solution is strongly acid, when the proportion of borax is greater the solution is alkaline (dulcitol being neutral and borax slightly alkaline). A solution of a mixture of dulcitol and sodium paratungstate has an acid reaction after boiling (Klein, Compt. rend, 99, 144).

Dulcitol sublimes partially on careful heating; at 200° it gives off water, and is converted into *dulcitan*; at 275° it decomposes.

Sodium, potassium, calcium, barium, and copper compounds exist.

Neither lead acetate nor subacetate precipitates dulcitol, but a white precipitate is thrown down with an ammoniacal solution of acetate. This is an unstable lead compound.

Dulcitol heated with hydriodic acid in an atmosphere of carbon dioxide yields hexyliodide, water, and iodine.

The hexanitrate is obtained by the action of fuming nitric and sulphuric acids on dulcitol. It crystallises from alcohol in beautiful colourless flexible needles, which melt between 68° and 72°, and give off nitric acid vapours continually, being thereby converted into the tetranitrate. This latter is soluble in alcohol, from which it crystallises in translucent prisms, m.p. 130°–140°, and decomposes at 145°.

Dulcitol forms with hydrochloric acid an unstable hydrochloride $C_6H_{14}O_6 \cdot HCl, 3H_2O$. Similar hydrobromides and hydroiodides exist; they are rather more stable (Bouchardat, Ann. Chim. Phys. [4] 27, 145).

Dulcitol yields chloro- and bromo- hydrins. $C_6H_{12}O_4Cl_2$ crystallises in tables insoluble in water: $C_6H_{12}O_4Br_2$ and $C_6H_{12}O_4BrCl$ are of much the same nature. The corresponding dulcitan bodies $C_6H_{11}O_4Cl$, &c., exist. When these bodies are dissolved in fuming nitric or sulphuric acids, the corresponding tetranitrates are formed, as $C_6H_8Cl_2(NO_3)_4$, &c.

With the acids of the fatty and aromatic groups, dulcitol forms a number of neutral compound ethers. Some of these are ethers of dulcitol and some of dulcitan.

The hexacetate forms hard crystalline plates, m.p. 171°; the hexabenzoate has m.p. 147°, both are insoluble in water and ether, sparingly soluble in cold alcohol.

The dibenzylidene acetal forms needles, m.p. 215°–220°. Dulcitol diacetone crystallises in prisms of bitter taste, m.p. 98°.

Dulcitol diacetone, m.p. 98°, may be fractionally crystallised into : Dulcitol α-diacetone, m.p. 145°–146°; and dulcitol β-diacetone, m.p. 113°–114°.

The α- form; when treated with benzoyl chloride and quinoline at 15°, gives monobenzoyldulcitol α-diacetone, an oil which, when shaken in chloroform solution with 5N/HCl, gives *monobenzoyldulcitol*, m.p. 155°–156°.

If the benzoylation is conducted at 100°, the first product is dibenzoyldulcitol α-diacetone, m p. 185°–186°, which with 5 p.c. HCl in cold acetic acid gives *dibenzoyldulcitol*, m.p. 210° (see E. Fischer, Ber. 1915, 48, 266).

Perseitol $C_7H_{16}O_7$ was discovered in the fruits of *Laurus persea*, and occurs in *Persea gratissima*. It is identical with *d*-mannoheptitol, synthesised by Fischer (Ber. 23, 930, 2226) by reducing the lactone of *d*-mannoheptonic acid. It crystallises in colourless slender needles, m.p. 188°; dissolves slightly in cold water (6 parts per 100); readily in hot water, and is insoluble in absolute alcohol. It has $[\alpha]_D - 1\cdot3°$, but becomes slightly dextro-rotatory in presence of borax.

Dilute nitric acid in the cold converts it into mannoheptose; the sorbose bacterium oxidises it to a ketoheptose.

The heptanitrate forms needles, m.p. 138°; the heptaacetate has m.p. 119°.

The optical isomeride of perseitol has not been found naturally, but is prepared artificially from *l*-mannoheptose.

Volemitol $C_7H_{16}O_7$ was obtained by Bourquelot by extracting dried *Lactarius volemus* with alcohol. It crystallises in slightly sweet slender needles, m.p. 151°–153°, $[\alpha]_D + 1\cdot92°$, which is not altered on the addition of borax. The constitution is not yet determined.

An **octitol** $C_8H_{18}O_8$ was obtained by Vincent and Meunier (Compt. rend. 127, 760) from the mother liquors of the sorbitol preparation from the fruit of some of the *Rosaceæ*. The syrup had $[\alpha]_j - 3\cdot42°$; the compound with benzaldehyde crystallised in slender needles, m.p. 230°; an isomeride formed at the same time having m.p. 140°.

THE DISACCHARIDES.

The disaccharides consist of two monosaccharides, united through an oxygen atom. One residue is fixed through the oxygen of the aldehyde group in just the same manner as is dextrose in the glucosides. In the second residue, the aldehyde or ketonic group may be still present, in which case the junction takes place through one of the alcohol groups, or it may have disappeared, being concerned in the junction. The disaccharides are accordingly of two types. In the first type, in which the aldehyde group is present, they reduce cupric salts, and behave just as dextrose does. In the second type, all these properties are absent. Most of the best-known disaccharides are derived from hexoses.

In establishing the structure of a disaccharide, three points demand attention: (1) the nature of the constituent hexoses; (2) whether it represents an *g*- or β-glucoside; (3) which hydroxyl- group is concerned in the attachment of the two hexose residues. As a rule, they form no really characteristic derivatives, so that

their isolation and identification is far from easy. Those of Type I. contain, like dextrose, an aldehyde group or its equivalent, and since they exhibit muta-rotation and exist in two modifications, there is no doubt that, like dextrose, they possess a closed ring structure rather than a free aldehyde group. In solution, therefore, they exist as an equilibrated mixture of interconvertible isomerides. This is in agreement with their crystallising properties and in marked contrast to the carbohydrates of Type II., *e q.* sucrose and trehalose, of which only one form exists, and which are characterised by crystallising readily.

Accordingly, both halves of the molecule possess a γ-oxidic structure, but only one section retains the aldehydic grouping potentially functional.

The disaccharides are selectively hydrolysed by enzymes, and are attacked with very different degrees of readiness by mineral acids.

Important conclusions as to their structure are based on this behaviour, for the full discussion of which reference should be made to The Simple Carbohydrates, by E F. Armstrong, ch. v. and vi. (Longmans, 1919)

The following table gives a list of the di, tri-and tetra-saccharides and their products of hydrolysis :—

DISACCHARIDES.

Carbohydrate	Components
Type I. *Aldehyde group, potentially functional*	
Maltose	Dextrose-α-glucoside
*Iso*maltose	Dextrose-β-glucoside
Gentiobiose	Dextrose-β-glucoside
Cellose	Dextrose-β-glucoside
Lactose	Dextrose-β-galactoside
*Iso*lactose	Dextrose-galactoside
Melibiose	Dextrose-galactoside
Turanose	Dextrose and levulose
Vicianose	Dextrose and arabinose
Galactobioses	Galactose-galactosides

Type II. *No reducing properties.*

Sucrose	Dextrose and levulose
Trehalose	Dextrose (2 mols.)
Glecoxylose	Dextrose and xylose

TRISACCHARIDES.

Type 1.

Mannotriose	Dextrose and galactose (2 mols)
Rhamninose	Dextrose and rhamnose (2 mols.)

Type II.

Raffinose	Galactose and dextrose and lævulose
Gentianose	Dextrose (2 mols.) and lævulose
Melezitose	Dextrose (2 mols.) and lævulose

TETRASACCHARIDES.

Type K.

Stachyose	Lævulose and dextrose and galactose (2 mols.)

Sucrose, Saccharose or **cane sugar.** The preparation and properties of this are dealt with under sugar, accordingly only the more theoretical aspects of its properties will be considered here. In contrast to most of the sugars it crystallises

exceedingly well ; this is almost certainly due to the fact that one substance only is present in solution, and not a mixture of isomerides. It lacks both aldehydic and ketonic properties, being without action on Fehling's solution. Considerable difficulty has been experienced in ascribing a constitutional formula to sucrose which is entirely satisfactory. It is probably a derivative of α-glucose, but since it is not attacked by maltase, it is not a simple α-glucoside. The methyl fructosides of the butylene oxide type are not attacked by invertase, and are far more stable to acids than sucrose. These facts are far more in agreement with the assumption that the fructose in the disaccharide has an ethylene oxide structure,' and this is confirmed by the hydrolysis of octamethyl sucrose to tetramethyl glucose and tetramethyl fructose. The former was of the stable butylene oxide type, the latter of the reactive ethylene oxide type.

Sucrose may be formulated accordingly as

$$\text{OH·CH}_2\text{·CH(OH)CH·[CH·OH]}_2\overset{\overset{\displaystyle O}{\displaystyle\mid}}{\text{CH}}\text{ O—}$$
$$\text{—C(CH}_2\text{OH)·CH·[CH·OH]}_2\text{CH}_2\text{OH}$$

On hydrolysis of sucrose the following series of changes take place, the final products consisting of the equilibrium mixtures A and C together, probably, with a small proportion of B (*cf.* Haworth and Law, Chem. Soc. Trans. 1916, 109, 1314)

Sucrose→α-glucose + α-fructose ⇄ α-fructose
　　　↓↑　　　　↓↑　　　　↓↑
　　β-glucose　　β-fructose　　β-fructose
　　A Butylene-　B Ethylene-　C Butylene-
　　oxide forms.　oxide forms.　oxide forms.

Sucrose contains eight hydroxyl groups, as evidenced by the formation of octacetyl-, octanitro-, and octamethyl- derivatives. It forms saccharates $C_{12}H_{21}O_{11}Na$ with sodium or potassium hydroxides, and more complex saccharates with lime, strontia and baryta.

Lactose or **milk sugar** $C_{12}H_{22}O_{11}$ was first separated from whey by Fabriccio Bartoletti in 1619, and termed *nitrum seri lactis.* It is found in the milk of all mammals. Human milk contains from 5 to 8 p.c. of milk sugar, cow's and ewe's milk, from 4½ to 5 p.c. ; mare's and ass's milk, about 6 to 7 p.c. It has not been found in plants.

Lactose is hydrolysed by mineral acids to dextrose and galactose ; it is a β-galactoside, that is, the active aldehyde group is in the dextrose residue. It is uncertain whether the primary alcohol group or the α-secondary alcohol group of the dextrose molecule takes part in the union with the galactose residue. Accordingly, lactose has one of the following formulæ :—

$$\text{C}_6\text{H}_{11}\text{O}_5\text{—O·CH}_2\text{·CH(OH)·CH[CH·OH]}_2\text{CH(OH)}$$
$$\text{(1)}\qquad\text{O}$$

$$\text{C}_6\text{H}_{11}\text{O}_5\text{—O·CH[CH}_2\text{·OH]·CH[CH·OH]}_2\text{·CHOH}$$
$$\text{(2)}\qquad\text{O}$$

The following details of the manufacture of lactose from whey are given by Aufsberg (Chem. Zeit. 1910, 34, 885). Cheese makers usually send their supply of whey to a central factory, where the lactose is separated. Before the whey is concentrated, it is heated and treated with

from 1 to 3 p.c. of acid (whey vinegar), in order to coagulate any albuminous substances present. The whey is then concentrated at a temperature of from 60° to 70° under reduced pressure, until it contains about 60 p.c. of total solids ; the concentrated liquid is run into rectangular vessels, each holding about 700 litres and surrounded by a cold-water jacket, and after the lapse of 10 hours the thick liquid is stirred, this operation being repeated at intervals. At the end of 24 hours, the pasty mass is submitted to centrifugal action, the crude, moist lactose amounting to about 3·85 p.c. of the weight of the original whey ; a further quantity of crude lactose, amounting to about 0·5 p.c., is obtained by evaporating the mother liquor and allowing it to crystallise. The crude lactose is now re-fined by dissolving it in water so as to form a solution having a density of 13° to 15° B., adding to the solution a quantity of bone charcoal and about 0·2 p.c. of acetic acid, heating the mixture to 90°, then adding a small quantity of magnesium sulphate, and heating the whole to boiling. The flocculent precipitate is removed by filtration, and the filtrate is evaporated by heating under reduced pressure until it has a density of 35° B. Crystallisation is then allowed to take place, and the crystals are separated. The lactose thus obtained is again subjected to a similar refining treatment, the final yield of crystalline lactose being dried in a centrifugal machine supplied with a current of hot air. The dry product, amounting to about 2·5 p.c. of the weight of the original whey, is then ground and sifted. *See* also MILK SUGAR.

Milk sugar is deposited from its aqueous solutions in hemihedral rhombic or monoclinic crystals. The crystals are white, semi-transparent, hard, and grate between the teeth ; their sp.gr. is 1·53–1·54. They contain 1 molecule of water ($C_{12}H_{22}O_{11},H_2O$), which they retain at 100° over H_2SO_4, but are given up completely at 130°, leaving a colourless melted mass of anhydrous milk sugar, which solidifies in the crystalline state on cooling, and is strongly hygroscopic.

If a solution of milk sugar is evaporated to dryness on the water-bath, an anhydrous milk sugar remains behind, which is not hygroscopic.

Hydrated milk sugar is slightly hygroscopic, soluble in 5 or 6 parts of cold or 2½ of boiling water ; from the latter solution the crystals only separate out slowly on cooling. An aqueous solution saturated at 10° has a density of 1·055, and contains 14·55 p.c. of hydrated milk sugar ; when left to evaporate it begins to deposit crystals as soon as the density = 1·063, and the solution contains 21·64 p.c. of sugar. It is insoluble in alcohol or ether.

According to Hudson (J. Amer. Chem. Soc. 1908, 30, 1767), lactose hydrate crystallises from aqueous solution at the ordinary temperatures, whilst above 95° the β-anhydrous form separates. Schmoeger, and later Hudson, have described three forms of lactose. The α-hydrate $[\alpha]_D+86°$ and the β-anhydride $[\alpha]+35·4°$ both change in solution into the equilibrium mixture or γ-isomeride of constant rotatory power $[\alpha]_D+55·3°$. Lactose was the first carbohydrate of which more than one modification was observed, and the relationship of these isomerides has been the

subject of much discussion (*see* v. Lippmann, Chemie der Zuckerarten). It is to be explained in the same way as the muta-rotation of dextrose.

Lactose loses the water of crystallisation at 130° when heated, turns brown at 160°, begins to decompose at 175° forming lactocaramel $C_{12}H_{20}O_{10}$, and melts at 203°.

On oxidation with bromine water, lacto-bionic acid, $C_{12}H_{22}O_{12}$ is formed, and this is converted into galactose and gluconic acid, when hydrolysed by boiling with mineral acids, proving that lactose is a galactoside. Nitric acid first causes hydrolysis, and then forms mucic acid from the galactose, and saccharic acid from the dextrose. Like dextrose, lactose gives rise to two series of derivatives, corresponding to the α- and β- forms of the sugar already mentioned. It contains 8 hydroxyl- groups, and therefore forms octacetates on heating with acetic anhydride and a dehydrating agent. These are colourless, crystalline substances, and well characterised. Other lower acetates are less definitely characterised.

Lactose octacetate may be converted into acetochlorolactose, and this into methyl lacto-side, which crystallises in needles, m p. 171°. The octacetate, obtained by heating with acetic anhydride, crystallises in rectangular plates or needles, m.p. 86° (Herzfeld), 98° (Kremann, Schmoeger), 106° (Fischer and Armstrong), according to the method of purification. It is obviously a mixture. Acetochlorolactose forms prisms, m.p. 57°–59° (Fischer and Armstrong, Ber. 35, 841), $[\alpha]_D^{20}+76·2°$. The isomeride forms prisms, m p. 118°–120°, $[\alpha]_D^{20}+73·5°$ (*see* also Bodart, Monatsh. 23, 1 ; Dittmar, *ibid.* 23, 865).

On heating with phenylhydrazine, acetic acid and sodium chloride in a boiling water-bath for 1½ hours, phenyllactosazone $C_{24}H_{32}O_9N_4$ is formed. This does not separate until the solution is cold, and is thus readily distinguished from phenylglucosazone. The yellow needles melt at 200°, and dissolve in 80 parts of boiling water. With very dilute sulphuric acid they form an anhydride $C_{24}H_{30}O_8N_4$, which melts at 223°–224°, and is almost insoluble in water (Fischer, Ber. 20, 830). The phenylhydrazine residues are eliminated by boiling with benzalde-hyde, lactosone being formed :

$$C_6H_{11}O_5 \cdot O \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot CHO$$
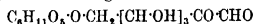
This is obtained as a colourless syrup on concen-tration of the aqueous solution in a vacuum, and is similar in properties to glucosone.

Lactose forms characteristic hydrazones with some of the substituted phenylhydrazines. The amylphenylhydrazone has m.p. 123° ; allyl-phenylhydrazone, m.p. 132° ; benzoylphenyl-hydrazone, m.p. 128° ; β-naphthylhydrazone, m.p. 203°. Lactal $C_{20}H_{18}O_9$, which is analogous to glucal from glucose, has m.p. 184°–186°, $[\alpha]_D+27°$.

Alkalis decompose lactose, giving a variety of products. Strong alkalis produce ultimately lactic acid ; on fusion with potassium hydroxide, oxalic acid is formed. The prolonged action of lime results in the formation of saccharins (*q.v.*).

Hydrolysis.—Lactose is hydrolysed with difficulty by cold mineral acids, and resists even

boiling with weak organic acids. Towards sulphuric acid it is 1240 times as stable as sucrose, and slightly more stable than maltose. Stronger acids hydrolyse it to dextrose and galactose, the optical rotatory power of the solution changing from $+52°$ to $+68°$.

Lactose is also hydrolysed by an enzyme lactase (q.v.) which is present in Kephir grains, in almonds, and in some yeasts. It is not fermented by yeasts, with the exception of a few torula (S. fragilis, &c.; see Armstrong, Proc. Roy. Soc. 1905, 76 B, 600) which contain lactase. It is more susceptible to bacterial attack, and readily undergoes lactic and butyric acid fermentations.

The synthesis of lactose has not been effected, but an isomeride named provisionally iso-lactose, was obtained by Fischer and Armstrong by the synthetical action of Kephir lactase on a concentrated mixture of equal parts of galactose and dextrose. It was isolated as phenyliso-lactosazone. A galactosidoglucose was prepared by the same workers from acetochlorogalactose, and shown to be probably identical with melibiose.

Maltose $C_{12}H_{22}O_{11}$ was perhaps obtained from starch by De Saussure in 1819; it was prepared by Varry, who failed to recognise it as a distinct substance. Dubrunfaut, in 1847, further examined it and gave the name maltose, but regarded it as a trisaccharide. O'Sullivan showed, in 1872, that it is a disaccharide, and gave a fuller description of its characters.

Maltose is primarily a decomposition product of starch, and its occurrence in nature is mainly under conditions where it has been derived from starch. Thus it is found in the leaves of plants, in germinating seeds, and in malt, &c. Under abnormal conditions, it is found in the urine. It is a constituent of commercial glucose. Its occurrence in the form of a glucoside is doubtful; amygdalin does not contain maltose, and it is improbable that lotusin does.

Starch is converted by the enzyme diastase first into dextrins and then into maltose. Diastase also acts on glycogen, forming maltose amongst other products. It is also obtained when starch is hydrolysed by acids. Early workers have denied the presence of maltose amongst the products of acid hydrolysis, but Fernbach and Schoen (Bull. Soc. chim. 1912, 11, 303) have completely identified it. They regard the processes of hydrolysis of starch by diastase and by acids as essentially identical in the first stage.

Preparation.—Maltose is always prepared by the action of diastase, usually malt extract, on starch paste; its purification from the dextrins present, which are soluble in alcohol, is often a matter of difficulty. Baker and Day (Brit. Ass. Report, Dublin, 1908, 671) recommend the use of ungerminated barley diastase, which converts starch into maltose, about 60 p.c., and a-amylodextrin: this can easily be separated by one precipitation with alcohol. Precipitated barley diastase is added to a 3 p.c. starch paste, and hydrolysis conducted at 50° for 5 or 6 hours, and subsequently in the cold. The solution is evaporated to a thin syrup and poured into 95 p.c. cold alcohol, so that the resulting strength is about 80 p.c. The a-amylodextrin is precipitated and removed by filtration. The alcohol is

distilled off the maltose syrup, seeded with a few crystals, and a little alcohol added. In a few hours it sets to a solid magma of pure maltose. To purify it further the sugar is triturated with strong alcohol, filtered, dissolved in a little water, and poured into boiling 95 p.c. alcohol, again filtered and crystallised from the filtrate.

When malt diastase is used, the procedure is similar, but the entire removal of admixed dextrins requires repeated purification. Maltose of this degree of purity separates readily from strong aqueous solution.

Properties.—Maltose crystallises from water in plates which contain $C_{12}H_{22}O_{11},H_2O$; from alcohol (sp.gr. 0·810) it crystallises in crusts, and at times in cauliflower-like or warty aggregations which contain $C_{12}H_{22}O_{11}$. The hydrate easily parts with its water at 100° in a current of dry air. The anhydride is but slightly soluble in strong ethyl alcohol; it is more soluble in methyl alcohol. The hydrate dissolves more freely in both solvents. Both bodies are very soluble in water, but less so than dextrose. The solution is optically active, the activity being less when the solution is freshly prepared than after standing.

The specific rotatory power for dry maltose is $[a]_j^-$ 154°–155°, $[a]_D^-$ 139°–140° at 15·5° in solutions containing 10 grams per 100 c.c. and under (O'Sullivan, Chem. Soc. Trans. 35, 771, and 45, 5). Meissel (J. pr. Chem. [2] 25, 114) gives the formula

$$[a]_D = 140·375° - 0·01837P - 0·095T$$

to represent the specific rotatory power of dry maltose at 0°, in which P = percentage of maltose in solution, and T the temperature of observation. Brown, Morris, and Millar give $+137·93°$. The value depends on the concentration as well as on the temperature. The initial rotation is $[a]_D = +119°$. Brown and Morris have shown that maltose is first formed in this low rotatory modification.

Maltose reduces Fehling's solution, 100 parts being equivalent to 62·5 parts of dextrose (O'Sullivan), or 61·9 parts (Brown and Heron, Chem. Soc. Trans. 1879, 35, 618). It is inactive towards cupric acetate (Barfoed's reagent). The density of a solution containing 10 grams maltose in 100 c.c. at 15·5° is 1·0393.

Maltose is hydrolysed on heating with mineral acids to two molecules of dextrose. Sulphuric acid at 80° attacks it 1·27 times as readily as lactose. The weaker organic acids are almost without effect except after prolonged action.

Bromine oxidises maltose to maltobionic acid (Fischer and Meyer, Ber. 22, 194). This has the formula $C_{12}H_{22}O_{12}$, and is hydrolysed by mineral acids to dextrose and gluconic acid. The behaviour towards maltase classes maltose as dextrose-a-glucoside, and the following constitutional formula is provisionally applied:—

$$CH_2(OH)\cdot CH(OH)\cdot CH\cdot[CH\cdot OH]_2\cdot CH$$
$$CH(OH)\cdot[CH\cdot OH]_2\cdot CH\cdot CH(OH)\cdot CH_2$$
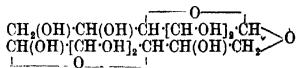
The compounds of Maltose.—The octonitrate (Will and Lenze, Ber. 31, 68) crystallises in

lustrous needles, m.p. 163°–164°, $[\alpha]_D^{20}+128°$
The octacetate exists in two isomeric forms.
Prepared by heating maltose with acetic anhy-
dride and sodium acetate, it has m.p. 159°–160°,
$[\alpha]_D+63°$ in chloroform. The α-isomeride has
m.p. 125°, $[\alpha]_D+122°$ (Hudson and Johnson,
J. Amer. Chem. Soc. 1915, 37, 1276).

α- and β-heptacetylchloro- and -bromo-
maltose have been described (Fischer and Arm-
strong, Ber. 34, 2895 ; 35, 840 ; Foerg. Monatsh.
23. 44).

α-Methyl maltoside (Foerg, ibid. 23, 44)
crystallises in slender plates, m.p. 125°–127°.
β-Methyl maltoside (Fischer and Armstrong,
Ber 13, 34, 2895 ; König and Knorr, ibid. 34,
4343) forms concentrically grouped needles,
m.p. 93°–95°, $[\alpha]_D^{20}+70°$. β- Phenyl maltoside,
m.p. 96°, and menthyl maltoside (Fischer, Ber.
1910, 43, 2521), have also been described.

The hydrazones are not characteristic.

The phenylosazone $C_{24}H_{32}O_9N_4$ is prepared
by heating maltose with excess of phenylhydra-
zine and acetic acid for 1½ hours on the water-
bath. It separates after the solution has cooled
(difference from dextrosephenylosazone). Ac-
cording to Fischer (Ber. 17, 579 ; 20, 821) it
crystallises in slender bright yellow needles and
not in aggregates, having in p. 206° ; Ost (Chem.
Zeit. 19, 1503) gives 202°–208°.

J. L. Baker states that the osazone prepared
from his pure maltose had m.p. 195°, and con-
sisted entirely of characteristic broad prisms,
resembling ribbons in the microscope field.
The stellate aggregates of crystals present in
the osazone, from maltose containing traces of
dextrin, were absent. Maltosazone does not
form an anhydride

Maltose-*p*-bromophenylosazone has m.p.
198°. The *p*-nitrophenylosazone crystallises in
red needles, m p. 261° (Hyde, Ber. 32, 1815).

Maltose-*p*-diaminobenzoic acid

$$C_6H_3(CO_2H)\underset{NH}{\overset{NH}{\diagup\!\!\!\diagdown}}C_{12}H_{20}O_{10}$$
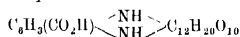
is formed in small quantities on prolonged
boiling of concentrated solutions of the com-
ponents. It crystallises anhydrous in plates,
m.p. 235°, or hydrated with 1 mol. H_2O in needles.
The metallic compounds of maltose are amor-
phous and ill-characterised. It does not form
double salts with the alkali chlorides.

Fermentation.—Maltose is fermented only
after hydrolysis to dextrose. This hydrolysis
is effected by maltase, which is present in most
yeasts but absent in *S. Ludwigii, S. Marxianus,
S. exiquus, S. membranæfaciens,* some forms of
S. anomalus, W. saturnus, and many others.
Accordingly, these yeasts do not ferment
maltose. Maltose is also fermented by most
moulds, and readily undergoes lactic and butyric
acid fermentation.

Synthesis.—Maltose is perhaps formed to-
gether with *iso*maltose by the action of concen-
trated hydrochloric acid on dextrose. It is also
formed by the action of emulsin on concen-
trated solutions of dextrose (E. F Armstrong,
Proc. Roy. Soc. 1905, 76 B, 592). In each case,
however, only amorphous or syrupy products
could be obtained.

Isomaltose (Revertose, Gallisin) was obtained

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by Fischer (Ber. 23, 3024, 3687) by the action of
400 grams of cold concentrated hydrochloric
acid on dextrose (100 grams) at 10°–15°. It is
a viscid syrup, $[\alpha]_D+70°$, and characterised by
being non-fermentable and forming a crystalline
phenylosazone, m.p. from 140° to 155° (Fischer),
according to the purity.

Scheibler and Mittelmeier (Ber. 23, 3075)
claimed that the gallisin of Schmitt and Cobenzl
(Ber. 17, 1000, 2456) consists mainly of
*iso*maltose.

Gallisin is found in commercial glucose. It
may be obtained as a white amorphous deli-
quescent powder, by treating the unfermentable
syrup, after evaporation, with absolute alcohol,
and finally with ether alcohol. It has a slightly
sweet taste ; is insoluble in ether, slightly
soluble in absolute ethyl alcohol, more easily
soluble in methyl alcohol and acetic acid. It
reduces silver nitrate, and Fehling's solution ;
the cupric reducing power of 10·98 grams=that
of 5 grams of glucose. It gives no precipitates
with solution of lead acetate, mercuric chloride,
ferric chloride, or barium chloride. On boiling
with dilute acids it is converted into dextrose.

Subsequently, a large number of products
obtained in the hydrolysis of starch or of
glycogen have been stated to be identical with
*iso*maltose, but, failing any characteristic deriva-
tive, definite proof of its presence in such cases
is lacking (*v.* Lippmann's Chemie der Zucker-
arten). It is possible that gallisin and most of
these products represent dextrins of low molecular
weights or admixtures of these with maltose.

By the action of maltase on a concentrated
solution of dextrose, Croft Hill (Chem. Soc.
Trans. 1903, 83, 578) has obtained a disaccharide
which he terms Revertose. Possibly this is
identical with *iso*maltose.

By a similar process, E. F. Armstrong (Proc.
Roy. Soc. 1905, 76, B, 592) has obtained an
*iso*maltose which, like that obtained by the
action of acids, is hydrolysed by emulsin.
*iso*Maltose is not attacked by maltase, and the
behaviour towards enzymes suggests that it is
dextrose-β-glucoside.

According to Gatterbauer (Zeitsch. Nahr.
Genussm. 1911, 22, 265), the difficultly ferment-
able part of starch-syrup, formerly termed
gallisin, consists of a new carbohydrate *glucosin*
and small amounts of maltose ; dextrins are
not present.

Glucosin is isomeric but not identical with
maltose ; it is a yellowish-white powder,
hydrolysed with difficulty by beer-yeast, more
readily by yeast maltase or emulsin, to glucose.

Dilute mineral acids give glucose, with
concentrated mineral acids the reaction is
reversible. The *phenylosazone* melts at 97°–
100°, the *p*-nitrophenylosazone at 240°.

Cellose (*Cellobiose*) is prepared by hydrolysis
of the octacetate formed by the action of acetic
anhydride on filter paper.

To prepare the octacetate $C_{12}H_{14}O_{11}(OC_2H_3)_8$,
7·5 grams of finely divided filter paper are
shaken with 20 c.c. acetic anhydride, the mixture
cooled to 70°, and at this temperature a mixture
of 7 c.c. acetic anhydride and 4 c.c. concentrated
sulphuric acid is added. The temperature rises
to 110°, the product is poured into 500 c.c. water,
and the amorphous acetate collected, washed,
and repeatedly crystallised from 95 p.c. alcohol

B

or from ethylacetate. It is ultimately obtained in colourless needles, m.p. 228°.

Five grams are moistened with alcohol and hydrolysed with 15 p.c. alcoholic potassium hydroxide. A granular powder separates: this is dissolved in a little water, excess of alkali neutralised with acetic acid, and the solution evaporated to a syrup, which, after treatment with absolute alcohol and inoculation with a crystal, ultimately yields cellose as a colourless microcrystalline powder. It tastes faintly sweet, dissolves in 8 parts of cold and 1·5 parts of hot water, and reduces Fehling's solution. It has $[a]_D^{20}$ about $+25°$ when freshly dissolved, increasing to $+35·0°$. It is not fermentable; acids hydrolyse it to 2 molecules of dextrose, as also does the emulsin of almonds

The phenylosazone forms long yellow needles, m.p. 208°–210°, $[a]_D$ −17·5°, soluble in 135 parts of boiling water.

Hudson and Johnson (J. Amer. Chem. Soc. 1915, 37, 1276) consider that cellose is composed of two glucose residues united similarly to the glucose and galactose residues in lactose. They quote an a-octacetate, m.p. 229°, $[a]_D + 42°$, and a β-octacetate prepared with acetic anhydride and sodium acetate, m.p. 202°, $[a]_D$ −15°. On reduction of ocetobromocellose with zinc and acetic acid and hydrolysis of the acetyl derivative cellobial is obtained, m.p. 175°–176°, $[a]_D + 1°$. Emulsin hydrolyses this to glucose and hydroglucal (Fischer and Fodor, Ber. 1914, 47, 2057).

Hudson and Dale (l.c.) give the specific rotation in water of the a- and β- forms of cellose as $+72·0°$ and $+16·0°$ respectively.

Gentiobiose is obtained by the action of invertase or of very dilute acids on the trisaccharide gentianose. It may be prepared from old gentian roots in which this hydrolysis has already taken place by the extraction with water and removal of the laevulose by fermentation with top-fermentation yeast. It separates from alcohol in anhydrous crystals, m.p. 190°–195°. It exhibits muta-rotation, the initial value for $[a]_D^{20}$ being $+9·6°$. It is not fermented by yeast. Emulsin, derived either from almonds or Aspergillus niger, hydrolyses it to dextrose. The phenylosazone has m.p. 142°.

The β-octacetate, m.p. 195°, $[a]_D$ −6°, crystallises well, and may be used to isolate gentiobiose from gentian roots or other plant products The phenylosazone crystallises in stellate needles, m.p. 160°–170°, $[a]_D$ −76°. An isomeride obtained on heating this with acetic anhydride and zinc chloride has m.p. 188°–189°, $[a]_D + 52°$.

Melibiose was first obtained, together with laevulose, by the partial hydrolysis of raffinose (Scheibler and Mittelmeier, Ber. 22, 1678, 23, 1438); this may be effected by dilute acids or certain bottom-fermentation yeasts. Bau gives the following methods of preparation.

20 grams of raffinose in 250 c.c. water are sterilised and fermented for 1 day at 30° with a pure culture of a top-fermentation yeast. The filtrate is sterilised and fermented during several days with a further portion of the yeast. It is

then concentrated, poured into hot alcohol, and, after cooling, precipitated with ether. This syrup, after further treatment with alcohol and inoculation, crystallises with difficulty after long standing in the cold (cf. also Hudson, J. Amer. Chem. Soc. 1915, 37, 2734).

Alternatively, 20 p.c. solutions of raffinose are hydrolysed by boiling with 2 p.c. acetic acid, and concentrated to a syrup in a porcelain vessel. This is rubbed with 2 vols. of 95 p.c. alcohol, the alcohol decanted, and ether added till a cloud appears. After 2 days, this solution is decanted from any precipitate, inoculated with a few crystals, and set aside in closed vessels.

Melibiose hydrate $C_{12}H_{22}O_{11},2H_2O$ forms doubly refractive monoclinic plates:

$$|a \cdot b : c = 1 : 1·9227 : 2·0124, \beta = 77·16°|$$

m p. 84°–85°. The hydrate has $[a]_D^{20} + 129·5°$ as stable value, and shows muta-rotation, the initial value, 5 minutes after solution, being $+108°$. The anhydride has $[a]_D^{20} + 143°$. It is very soluble in water, sparingly so in ethyl alcohol Strong acids hydrolyse it to dextrose and galactose: it is slightly more resistant than lactose. It is very sensible to traces of alkali. It is reduced by sodium amalgam to melibiositol, a syrup which is hydrolysed to galactose and mannitol. It is attacked by bottom- and not by top-fermentation yeasts, and thus affords a means of distinguishing between these two varieties of yeast The former variety contains the enzyme melibiase. It is slowly hydrolysed by emulsin.

The following derivatives are known: phenylhydrazone, light-yellow needles, m p. 145°; allylphenylhydrazone, m.p. 197°; β-naphthylhydrazone, m.p. 135°; phenylosazone, yellow needles from toluene, m.p. 178°–179°. This dissolves in 110 parts of boiling water, and interacts with benzaldehyde to form melibiosone. The p-bromophenylosazone has m.p. 181°–182°. The octacetate has m.p. 177°, $[a]_D + 102°$.

Melibiose was the first natural disaccharide to be obtained synthetically (Fischer and Armstrong, Ber. 35, 3144). It was prepared by the interaction of acetochlorogalactose with dextrose.

Trehalose (mycose, trehalubiose) was originally discovered in ergot, and has since been proved to be very widely distributed in fungi (Bourquelot). It apparently replaces sucrose in those plants which contain no chlorophyll and do not manufacture starch. Trehalose was found in 142 out of 212 species investigated, but only in certain parts of the fungus and at certain stages of the vegetative period. The quantity is a maximum just before the formation of spores. When fungi are picked, trehalose is rapidly converted into mannitol, and after a few hours it has entirely disappeared. The trehala manna from Syria and Persia is stated to contain 20 p.c. of trehalose. To prepare trehalose, suitable fungi (particularly Agaricus and Boletus species) are boiled with much strong alcohol immediately after picking. It was found as an incrustation on flowers of Carex brunescens (flowering rush) after a sudden sharp July frost (von Lippmann, Ber. 1912, 45, 3431).

**Trehalose** $C_{12}H_{22}O_{11},2H_2O$ crystallises in lustrous glass-like rhombic prisms

$[a : b : c = 0.6814 : 1 : 0.4171 ; \beta = 111° 31']$

m.p. 97°. It becomes anhydrous at 130°. It has $[a]_D^{20} + 178°$ for the hydrate and $+197°$ for the anhydride, without any muta-rotation. Acids hydrolyse it to 2 molecules of dextrose, but according to Winterstein, only with considerable difficulty, and it contrasts markedly in this respect with sucrose.

It does not reduce Fehling's solution or form a phenylosazone, and has the formula

$$\overset{\bullet O\text{——}}{\underset{\text{CH}_2(\text{OH})\text{·CH(OH)·CH·CH(OH)·CH(OH)·CH}}{\text{CH}_2(\text{OH})\text{·CH(OH)·CH·CH(OH)·CH(OH)·CH}}}\!\!>\!\!O$$
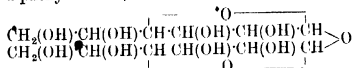
It is not hydrolysed by invertase and most enzymes, but is affected by a special enzyme, named trehalase, present in most fungi, moulds, and some yeasts, and conveniently prepared from *Aspergillus niger*. Accordingly, trehalose is fermented by those yeasts which contain trehalase. It forms few derivatives: the octanitrate has m.p. 124°, $[a]_D^{18} + 173.8°$; the octacetate has m.p. 97°, $[a]_D + 162°$; the tetrabenzoate, m.p. 81°–83°.

Turanose $C_{12}H_{22}O_{11}$ is obtained from the trisaccharide melezitose, together with dextrose on hydrolysis with 20 p.c. acetic acid solution. The dextrose is destroyed by yeast, and the turanose isolated from an alcoholic extract of the residue in transparent non-crystalline rounded grains of the composition

$$C_{12}H_{22}O_{11} \cdot \tfrac{1}{2}C_2H_6O.$$
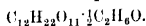
They melt at 60°–65°, lose their alcohol at 100° and yield the pure sugar $[a]_D + 7.18°$ without muta-rotation (Tanret, Compt. rend. 1906, 142, 1424).

Turanose has a reducing power of 60 (dextrose = 100), and is hydrolysed by mineral acids to an equal molecular mixture of dextrose and lævulose, and not to dextrose only, as originally stated by Alekin (Ann. Chim. Phys. [6] 18, 532). Invertase, maltase, emulsin, and diastase are without action. The phenylosazone has m.p. 215°–220° (Fischer, Ber. 27, 2486). It thus differs from sucrose in containing a free aldehydic group.

OTHER LESS-KNOWN DISACCHARIDES.

Glucoapiose $C_{11}H_{20}O_{10}$ is contained in the glucoside apiin. It has not yet been isolated, as hydrolysis of apiin by dilute acids yields only apiose and gluco-apigenin, and enzymes are without action.

Galacto-arabinose was obtained by Ruff and Ollendorf (Ber. 32, 352 ; 33, 1806) by oxidation of lactobionic acid from lactose. It is a dextrorotatory syrup : the phenylosazone has m.p. 238°.

Glucoxylose. By hydrolysis of the glucoside *dibenzoylglucoxylose*, occurring in *Daviesia latifolia*, the carbohydrate *glucoxylose* $C_{11}H_{20}O_{10}$, is produced as an amorphous horny mass, very soluble in water (Power and Salway, Chem. Soc. Trans. 1914, 105, 767, 1062). It has $[a]_D - 36°$, does not reduce Fehling's solution, and does not

give an osazone. Acid hydrolysis yields glucose and xylose. Its constitution is therefore given as :—

$$CH_2(\text{OH})\text{·CH(OH)·CH·[CH(OH)]}_2\text{·CH·}$$
$$\underset{\text{——O——}}{}$$
$$O\text{—CH·[CH(OH)]}_2\text{·CH·CH}_2(\text{OH})$$
$$\underset{\text{——O——}}{}$$
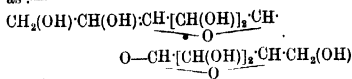
Strophantobiose $C_{12}H_{22}O_{10}$ is obtained in the form of the methyl-derivative from the glucoside strophantin (Fiest, Ber. 31, 535 ; 33, 2063, 2069, 2091). It forms colourless crystals, m.p. 207° ; does not reduce Fehling, and is not fermentable. Acids hydrolyse it to mannose, rhamnose, and methyl alcohol.

Vicianose $C_{11}H_{20}O_{10}$ is prepared by Bertrand and Weisweiller (Compt. rend. 1910, 150, 180) by hydrolysing the glucoside in the seeds of *Vicia angustifolia* by the enzyme occurring in them. It crystallises in aggregates of small needles, m.p. about 210° ; has $[a]_D^{20} + 39.7°$, the initial value being much higher. It reduces Fehling, and is converted into dextrose and arabinose on hydrolysis.

Diglucose from amygdalin. When amygdalin is hydrolysed by the digestive juice of *Helix pomatia*, the first product is a biose obtained as an amorphous powder. This is nonfermentable, and does not reduce Fehling's solution : it probably has a constitution resembling that of trehalose (Guaja, Compt. rend. 1910, 150, 793–796).

TRISACCHARIDES.

Mannotriose $C_{18}H_{32}O_{16}$ is obtained by the action of either invertase or acetic acid on mannotetrose (stachyose). It is a colourless, faintly sweet crystalline substance, m.p. 150° $[a]_D + 167°$. It reduces Fehling's solution. Bromine oxidises it to mannotrionic acid, which is hydrolysed on warming with acids to 2 mols. *d*-galactose and 1 mol. gluconic acid. It is slowly hydrolysed by emulsin and by some yeasts, and is then fermented, but whether completely so is not known.

The phenylosazone has m.p. 192°–194°, according to Neuberg, and 122° as given by Tanret. Bierry (Compt. rend. 1911, 152, 465) confirms m.p. 122°–124°.

Rhamninose $C_{18}H_{34}O_{14}$ is obtained from the glucoside xanthorhamnin present in the Persian berry (*Rhamnus infectoria*). In addition to the glucoside, the fruits contain an enzyme, termed rhamninase, which hydrolyses it to the trisaccharide and rhamnetin. Rhamninose forms colourless crystals of faintly sweet taste, m.p. 135°–140°, $[a]_D - 41°$; it reduces Fehling's solution. Acids hydrolyse it to galactose and 2 molecules of rhamnose. Sodium amalgam reduces it to the alcohol rhamninitol $[a]_D - 57°$, which is hydrolysed by acids to dulcitol and 2 molecules of rhamnose. Bromine oxides it to rhamninonic acid $C_{18}H_{32}O_{15}$, which is obtained, mixed with its lactone, as an amorphous substance ; m.p. 125°, $[a]_D - 94.3°$. It is hydrolysed to *d*-galactonic acid and rhamnose.

This behaviour points to the two rhamnose residues being united in the trisaccharide, but this disaccharide has not been isolated. Rhamninose

is not fermentable, and enzymes are without action. The octacetate has m.p. 95°, $[a]_D-31°$.

Gentianose $C_{18}H_{32}O_{16}$ is found in the roots of a number of gentians, from which it is prepared by extracting the fresh roots with 95 p.c. alcohol. It crystallises in colourless plates, m.p. 209°–210°, tastes faintly sweet, and has $[a]_D+31·2°$ to $+33·4°$.
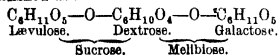
It does not reduce Fehling's solution, but is hydrolysed by acids to lævulose and 2 molecules of dextrose, the final product having $[a]_D-20·2°$. The enzyme invertase hydrolyses it to lævulose and the disaccharide gentiobiose, that of *Aspergillus niger* converts it into dextrose and sucrose.

Raffinose (also termed *melitose*, *gossypose*, *melitriose*) $C_{18}H_{32}O_{16}$ was first discovered by Johnston in 1843, in the manna from *Eucalyptus mannifera*, found in Tasmania. It is often found in considerable amount in the sugar beet, where it was discovered by Loiseau; Ritthausen found it in cotton-seed cake; it is also present in wheat and in oats. To prepare raffinose from molasses, strontium oxide is added until a molecule is present for every molecule of sucrose After some hours, the strontium saccharate formed is separated by filtration and the liquid heated with excess of strontia, whereby the raffinose distrontionate is precipitated. The strontia compound is decomposed by carbon dioxide, the solution concentrated, and the process repeated to remove most of the sucrose The syrup finally obtained is dissolved in hot alcohol; the product which separates on cooling is kept under alcohol in a closed vessel, when raffinose slowly crystallises.

According to Hudson and Harding (J Amer. Chem. Soc. 1914, 36, 2110), cotton-seed meal is extracted with water, and, after purification, the solution is evaporated and barium hydrate added. The barium raffinate is powdered and washed with methyl alcohol. The barium compound is suspended in water and decomposed with the exact amount of 50 p.c. phosphoric acid. The filtrate is completely freed from barium by sulphuric acid, and concentrated in a vacuum, seeded with raffinose hydrate and left to crystallise. The yield is 4–5 p.c. of the weight of cotton-seed meal employed.

Raffinose forms small needles, soluble in 6 parts of water at 16°; it is less soluble in ethyl alcohol than sucrose. It is difficult to recognise when it crystallises with sucrose. The hydrate melts at 80°, the anhydrous forms at 118°–119°. The optical rotatory power $[a]_D$ is $+104°$ without muta-rotation.

It has no reducing action, and behaves exactly as sucrose. Dilute mineral acids hydrolyse it to lævulose and melibiose: strong acids yield a molecule each of lævulose, dextrose, and galactose. Invertase converts it into lævulose and melibiose, emulsin hydrolyses it to sucrose and galactose. Accordingly, the formula is established as:

$$\underset{\text{Lævulose.}}{C_6H_{11}O_5}\text{—O—}\underset{\text{Dextrose.}}{C_6H_{10}O_4}\text{—O—}\underset{\text{Galactose.}}{C_6H_{11}O_5}$$
$$\underset{\text{Sucrose.}}{\qquad}\underset{\text{Melibiose.}}{\qquad}$$

The undeca-acetyl derivative has m.p. 100°, $[a]_D+92°$.

The analysis of raffinose in admixture with closely related sugars may be effected by means of selected enzymes. For details of the method, *see* Davis (J. Soc. Chem. Ind. 1915, 35, 201).

Melezitose (*melicitose*) $C_{18}H_{32}O_{16}·2H_2O$, is found in Briançon manna, which is obtained as an exudation from the young twigs of the larch (*Abies larix*; Fr. *Mélèze*). The manna from the Douglas fir consists mainly of melezitose (Hudson and Sherwood, J. Amer. Chem. Soc. 1918, 40, 1456). It was investigated by Berthelot (Ann. Chim. Phys. [3] 55, 282) and by Alekhine (*ibid* [6] 18, 532). It is found also in *turanbin* or *terenjabine*, an exudation from *Alhagi maurorum*, growing in Afghanistan, Persia, and in the deserts of the East, and used in Northern India as a laxative (Villiers, *ibid.* [5] 12, 43). This substance is a brown, semisolid mass, of a slightly sweet taste, due mainly to the presence of dextrose. To obtain melezitose from this product it is treated with four times its weight of lukewarm water, and the liquid passed through a sieve to separate husks, leaves, &c., and after standing to allow of the deposition of earthy matter, it is evaporated to half its bulk. On standing for a few days, the greater part of the melezitose crystallises out. The crystals are redissolved in twice their weight of hot water, the solution heated on the waterbath, diluted with its own volume of alcohol, heated to boiling to separate earthy and coagulable matter, and filtered whilst hot. On cooling, melezitose separates out and may be obtained pure by two or three recrystallisations. It forms large rhombohedral prisms

$$C_{18}H_{32}O_{16}·2H_2O$$
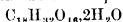
which effloresce in air and become opaque; they lose the whole of their water at 110°. Dehydrated melezitose has m.p 148°–150°; 100 pts. of water dissolve of anhydrous melezitose 26·8 pts. at 17.5°; 34·4 pts. at 25°; 75·6 pts. at 100°; sparingly soluble in alcohol, insoluble in ether. The rotatory power is $[a]_D+88·5°$. Melezitose yields no crystalline compounds with alkaline chlorides. On boiling with dilute sulphuric acid it yields *turanose* and dextrose, the rotation falling to $+63°$. It has no action on an alkaline solution of copper, and is unchanged by diastase or yeast. Nitric acid transforms it into oxalic acid without the intermediate formation of mucic acid. It does not interact with phenyl hydrazine. The undeca-acetate $C_{18}H_{21}O_{16}(OC_2H_3)_{11}$ crystallises in shining monoclinic prisms, m.p. 170°, $[a]_D^{20}+110·4°$.

Stachyose (*Mannotetrose, Lupeose*) $C_{24}H_{42}O_{21}$ was discovered by Schulze and Planta in the tubers of *Stachys tubifera*, and thought to be a trisaccharide. Tanret obtained it from ash manna, and termed it mannotetrose. It has also been found in the twigs of white jasmine and in the subterranean parts of *Lamium album*. It constitutes from 60–75 p.c. of the dry matter of the stachys tubers. The tetrahydrate crystallises in lustrous hard doubly refractive colourless plates ($a:b:c=1·0512:1:0·4213$, $\gamma=90°$ 46'). It tastes quite sweet and dissolves at 13° in 0·75 part of water. The anhydride has m.p. 167°–170°, $[a]_D+148°$, without muta-rotation; the hydrate has $[a]_D+133°$.

Stachyose is not acted on by Fehling's solution or by alkalis. Acetic acid hydrolyses it

to lævulose and mannotriose. Sulphuric acid converts it into 4 monosaccharides, viz. : 1 molecule lævulose, 1 molecule dextrose, 2 molecules galactose. By the action of nitric acid, about 38 p.c. of mucic acid is formed. Invertase hydrolyses it to lævulose and mannotriose, which latter is slowly attacked by the emulsin of almonds or of *Aspergillus niger*.

According to recent work of Schulze, stachyose is probably identical with the carbohydrate lupeose, present in *Lupinus luteus* and *angustifolius*, as lupeose has $[\alpha]_D + 148°$, and gives the same products on hydrolysis.

Neuberg (Biochem. Zeitsch. 1910, 24, 173) prepares it by pressing the juice from the tubers, precipitating impurities with mercuric acetate, removal of the metal by hydrogen sulphide, neutralisation with ammonia, and concentration to a syrup, which is precipitated with alcohol The precipitate is dissolved in water, impurities precipitated with phosphotungstic acid, and the filtrate concentrated. Barium hydroxide and alcohol are added alternately. After 24 hours, the barium salt is collected, washed with alcohol, and decomposed by carbon dioxide. Reducing sugars are removed by this treatment and the stachyose readily crystallises

Polyamyloses have been obtained from potato starch paste by the action of *Bacillus Macerans* (Schardinger, Chem. Soc Abstr. 1912, i. 181 ; Pringsheim and Langhans, Ber. 1912, 45, 2533). Tetra-amylose $(C_6H_{10}O_5)_4$ or α-dextrin crystallises in colourless hexagonal plates, $[\alpha]_D + 128°$, hexa-amylose or β-dextrin forms rhombic crystals, $[\alpha]_D + 136°$. On acetylation hydrolysis of the dextrins takes place, and from the acetyl derivatives formed diamylose and triamylose were obtained These crystallise in needles, and do not reduce Fehling's solution. Rice starch gives similar definite polyamyloses on degradation (Pringsheim, Ber. 1914, 47, 2565).

POLYSACCHARIDES.

Glycogen $(C_6H_{10}O_5)n$, the reserve carbohydrate of the animal organism in which it appears to take the place of starch, is a regular constituent of all developing cells. It is present in the liver up to 10 p c. and in muscle.

Preparation.—Liver is finely minced and thrown into boiling water acidified with acetic acid. The coagulated proteins are filtered off, and the remaining proteins precipitated from the filtrate with trichloracetic acid or potassium mercuric iodide (Brucke's reagent). Glycogen is precipitated from the filtrate with alcohol.

Fresh finely minced liver is extracted for 2 hours with boiling 60 p.c potassium hydroxide. An equal volume of 95 p.c. alcohol is added to the clear filtrate, containing 15 p.c. KOH, and the precipitated glycogen washed with a mixture of 15 p.c. KOH and 2 vols. of 95 p.c. alcohol.

It is purified in either case by solution and reprecipitation with alcohol, and obtained as an amorphous snow-white powder $[\alpha]_D + 191°$, soluble in cold water, giving an opalescent solution. It is not fermentable, does not reduce Fehling's solution, and is not acted on by alkali, even by concentrated solutions at the boiling-point. With iodine it gives a brown-red colouration. Acids hydrolyse it ultimately to dextrose, but dextrins and maltose are formed as intermediate products. Diastase derived from either plants or animals also converts it into dextrins and maltose (*see* Tebb, Journ. of Physiol. 1898, 22, 423).•

Glycogen may be obtained from yeast free from nitrogen, yeast-gum, and ash (Harden and Young, Chem. Soc. Trans. 1912, 101, 1928). The crude preparation from yeast is freed from nitrogen and ash by repeated solution in water and reprecipitating with alcohol ; the yeast-gum is removed by dissolving the crude glycogen in water and saturating with ammonium sulphate several times. The last traces of ash are removed by several reprecipitations from water by alcohol.

To estimate glycogen, the tissue is minced and boiled 2–3 hours with 30 p.c. potassium hydroxide. The solution is diluted, filtered, and precipitated with alcohol. The glycogen is again dissolved in dilute alkali and precipitated with alcohol. Finally it is dissolved in water and estimated by hydrolysis with acids into dextrose (1 part = 0·927 part glycogen) or with the polarimeter.

A 5 p.c. solution of sterilised glycogen treated with a potato culture of *Bacillus macerans* at 37° C. gave two crystalline cyclic polysaccharides (*dextrin-β-* or *β-hexa-amylose* (25 p c) and *dextrin-a-* or *tetra-amylose* (75 p.c.)). *See* Pringsheim and Lichtenstein, Ber. 1916, 49, 364.

Inulin. Inulin is widely distributed as a reserve material in plants having tubers or tuberous or fleshy roots, particularly in the autumn in dahlia tubers, Jerusalem artichoke, chicory, garlic, onions, and other plants and bulbs.

To prepare it, a mash is made of the ripe tubers, a little calcium carbonate is added, and the mixture extracted with boiling water. The filtrate is frozen and the sediment which separates dissolved in hot water and again frozen. Tanret advises precipitation with barium hydroxide, decomposition of this precipitate with carbon dioxide and subsequent precipitation with 95 p.c. alcohol

Inulin, precipitated by alcohol, is a compact colourless powder, resembling starch. The molecular composition is uncertain, as the ordinary methods do not yield trustworthy results. Kiliani gives $(C_6H_{10}O_5)_6, H_2O$; Brown and Morris, $(C_6H_{10}O_5)_{12}, 2H_2O$; Düll, $(C_6H_{10}O_5)_{18}, H_2O$; Tanret, $(C_6H_{10}O_5)_{30}, 5H_2O$. It melts at 178°, having $[\alpha]_D - 38°$ to $-40°$, sp.gr. about 1·5. In cold water it is sparingly soluble, but very soluble in hot water, and readily forms supersaturated solutions. It is precipitated by alcohol, when the percentage of alcohol in the liquid reaches 65.

The barium salt $C_{36}H_{62}O_{31}, 3BaO$ (Tanret, Compt. rend. 116, 415) is insoluble.

Inulin is hydrolysed by boiling the aqueous solution under pressure, by dilute acids, and also by the enzyme inulase, discovered by Reynolds Green, which is usually present in the same plant when in the germinating condition, but inert in the resting stage. In every case, lævulose is the sole product of hydrolysis. Yeasts are without action.

A number of products are described as

lævulins and lævulans, which probably represent polymerides of lævulose of lower molecular weight than inulin.

Manna is the dried saccharine exudation from the stem of the flowering ash. *Fraxinus ornus* and *F. rotundifolia*, small trees cultivated for the purpose in Sicily. A vertical series of oblique incisions is made in the bark when the trees are about 10 years old, the juice slowly exudes and either dries on the stem (flake manna) or in wet seasons drops from the trunk, where it is caught upon tiles or cactus leaves, yielding an inferior variety. Flake manna is obtained in commerce in brittle stalactitic pieces, about 4–6 inches long and 1 inch wide. It is yellowish-white in colour, has a slight agreeable odour and a sweet taste. It is used as a gentle laxative for infants and children.

It consists principally of mannitol (70–80 p.c.) : other constituents are mannotetrose (12–16 p.c.), mannotriose (6–16 p.c.) which is formed from mannotetrose, and small quantities of hexoses

. The term is not restricted to the ash, and a number of saccharine exudations of varying origin and composition are classed as ' mannas.' Amongst these are the Persian and Turkestan manna, derived from *Alhagi maurorum* or *camelorum* ; the tamarisk manna, also of Persian origin, from the *Tamarix gallica* ; oak manna, procured from *Quercus vallonia* and *Quercus persicus* in Kurdistan ; Australian manna, *Eucalyptus viminalis* ; Briançon manna, from the larch, *Larix europæa* in Southern France ; Astragalus manna, from various species of astragalus in Persia.

Authorities.—E. von Lippmann, Die Chemie der Zuckerarten, 3rd ed. 1904 ; L. Maquenne, Les Sucres et leurs principaux dérivés, Paris, 1900 ; F. Frankland Armstrong, The Simple Carbohydrates, London, 1919 ; E. Fischer, Untersuchungen uber Kohlenhydrate, 1884–1908, Berlin, 1909. E. F. A.

CARBOLIC ACID. *Phenol* ($C_6H_5 \cdot OH$).

Occurrence and Formation.—Carbolic acid occurs in small quantities in castoreum (Wöhler, Annalen, 67, 360), in urine (Stadeler, *ibid.* 77, 18), and is a constant product of the putrefaction of albumen (Baumann, Ber. 10, 685). It is formed when organic substances are strongly heated, and is contained in the tars obtained by the dry distillation of bones, wood (Duclos, 'Annalen, 109, 163), shale (brown coal), and coal (Runge, Pogg. Ann. 31, 69 ; 32, 308 ; Laurent, Ann. Chim. Phys. [3] 3, 195).

The tar produced in gas manufacture was until the late war the chief source of carbolic acid. Owing to the demand for carbolic acid as a disinfectant and for the manufacture of dyes and explosives, it has become usual, in tar distillation, to collect a special fraction, the ' carbolic oil ' containing as much carbolic acid as possible before collecting the ' creosote oil,' which contains the other phenolic constituents of coal tar. The ' carbolic oil ' begins to come over when the specific gravity of the distillate attains that of water. According to Watson Smith (Chem. Soc. Trans. 1886, 21), ordinary Lancashire coal tar yields about 5 p.c. by volume of crude phenols, containing 65 p.c. by volume of carbolic acid crystallisable at ordinary temperatures.

Coke ovens are now constructed so that the tar produced during the coking of coal can be collected ; the following data, having reference to the percentage of carbolic acid in such tars, are given by Lunge (Coal Tar and Ammonia, ed. 1909), which has been largely drawn upon in the compilation and revision of this article : he says, ' The tar from Hussener's modification of the Carvès oven gave 1·37 p.c. of pure carbolic acid ; the tar from the Simon-Carvès oven gave 0·05 p.c. of crude carbolic acid ; and similar ovens working with another kind of coal and at higher temperature gave 0·305 p.c. of crude acid. The tar collected from blast furnaces, working with coal (raw) and also that obtained from Mond and Duff producers, contains a high percentage of phenolic constituents, but the quantity of carbolic acid present is very small.'

Carbolic acid can be obtained by fusing potassium benzenesulphonate with caustic potash ; the yield is proportional to the temperature and quantity of alkali employed, and is at best (96·23 p.c. of that theoretically possible), when 1 mol. prop. of the former is fused with 6 mol. props. of the latter at 252°. Caustic soda cannot be employed instead of potash, since only a poor yield is obtained by its use (Degener, 7 pr. Chem. [2] 17, 394).

Carbolic acid can also be obtained by heating the diazo- compounds of benzene with water.

Preparation —Carbolic acid is almost exclusively obtained from coal tar, and is worked up either from the special fraction known as ' carbolic oil ' or from the oils intermediate in specific gravity (sp.gr. 1·000 1·020) between the light and heavy oils, that is, distilling between 170° and 230°. The acid is present also in the creosote oils, distilling between 240° and 270°.

The preparation of carbolic acid from coal tar is effected by washing the oils obtained on distilling the tar with a solution of caustic soda, sp.gr. 1·075 1·100, when the tar acids are dissolved as sodium compounds and form a heavy solution upon which the now neutral oils float. It is not advisable to use a stronger solution of caustic soda, as in that case a considerable quantity of naphthalene would also be dissolved. If it is desired to extract carbolic acid only, without any of the higher homologues, the oils are often washed fractionally. For example, a quantity of caustic soda solution more than enough to extract all the carbolic acid but insufficient to take up all the cresylic acid, is employed, and the phenate of soda solution drawn off is used to wash another portion of oil when the cresylate of soda is decomposed and the cresylic acid is replaced by carbolic acid, and a solution consisting almost entirely of carbolate of soda is obtained.

Another method, suggested by Davis, is to employ, for the first wash, only one-third of the quantity of caustic soda required to extract all the tar acids when carbolic acid only is extracted. In many works, however, the whole of the tar acids contained in the light oil, carbolic oil, and creosote oil fractions are extracted, and after separating the tar acids in one of the ways about to be described, the mixture of carbolic and cresylic acids obtained is separated by fractional distillation. The phenate or carbolate of soda, drawn off from the oil is, in many cases, first purified by blowing steam through it. This

carries away naphthalene, neutral oils, and pyridine bases, and the blowing with steam is continued until the water condensing from the escaping steam ceases to have a milky appearance. The purified phenate of soda is then treated with an acid to decompose it and set free the tar acids which float on the surface and are either skimmed off or are separated in an apparatus similar to a Florentine receiver.

Formerly the decomposition was almost always effected by sulphuric or hydrochloric acid, in which case the soda was lost as sulphate or chloride, which it did not pay to recover. The more common practice to-day, however, is to use carbon dioxide to effect the decomposition. If this is used under pressure, complete decomposition is said to be effected, but more generally the process is completed by the addition of a small quantity of sulphuric acid ; thus is the more necessary, as both carbolic acid and carbolate of soda are mutually soluble in each other.

The separated solution of sodium carbonate, which contains about 1 p.c. of carbolic acid, is recausticised with lime and is used over again to wash another quantity of oil. A twofold saving is thus effected, in that the loss of the soda is avoided and also the carbolic acid which remained dissolved in the sodium sulphate or chloride solution, and was run to waste, is now recovered, inasmuch as it goes forward with the next washing operation. The crude carbolic thus obtained contains, besides phenol (carbolic acid), about 14 to 15 p.c. of water and variable quantities of cresylic acid. It occurs in commerce in three qualities, known as 75's, 60's, and 50's crude carbolic acid, and its value is determined by 'Lowe's' test. This is performed as follows : 100 c.c. of the crude tar acid is slowly distilled in an 8-oz. glass retort, and the receiver is changed when 10 c.c. of oil have come over ; these 10 c.c. are accompanied by a varying amount of water, and by reading the quantity of water obtained, the percentage of water is ascertained. The distillation is continued until 62½ c.c. have collected in the graduated tube which is used as a receiver ; the distillation is then stopped. The 62½ c.c. are then cooled, and a minute crystal of pure phenol is dropped into the tube, and the cooling continued until the contents begin to crystallise. The temperature is noted when the crystallisation appears to spread through the tube, and this is the measure of the quality of the carbolic acid.

The preparation of pure carbolic acid from the crude article is always commenced by a distillation in wrought-iron stills, formerly without a column, but at the present day fractionating columns are almost universally employed. The water comes over first and then the carbolic acid, which is collected apart, so long as it crystallises on cooling. Some uncrystallisable acid comes over next, and the distillation is then stopped and the residue is mostly pitch.

In some cases, a little strong sulphuric acid and potassium dichromate is added to the contents of the still. The condensing worm must be made of zinc, silver, or stoneware. The distillate is allowed to cool and crystallise, and the crystals are drained from the liquid portion, either on a drainer or in a centrifugal machine. The liquid portion is either sold as liquid carbolic acid or is worked up again with the next batch. The drained crystals are treated with a small quantity of concentrated sulphuric acid and potassium dichromate* and redistilled, when ' pure ' crystallised carbolic acid of commerce is obtained. In some cases the separation of the last traces of cresylic acid is effected by adding a small quantity of water, and the mixture is cooled, when a hydrate of carbolic acid crystallises out ; this is separated from the liquid portion, which contains the cresylic acid and the crystals are redistilled. Water comes over first, and then the boiling-point rises and pure carbolic acid distils over. For medicinal purposes, a final distillation in glass retorts is performed.

Properties.—Pure carbolic acid crystallises in long, colourless needles ; has a characteristic odour ; melts at 42·5° or 43° and boils at 178·5° (Choay, Compt. rend. 118, 1211) ; Lunge (Coal Tar and Ammonia, 1909 ed. 210), gives m.p. 42·2° and b.p. 184° under 760 mm. pressure. Ordinary pure carbolic acid of commerce, which contains traces of cresols, melts at a somewhat lower temperature and boils at 182° to 184°. The specific gravity of carbolic acid at 18° is 1·065 (Laurent) ; its expansion for temperature t° at 760 mm. pressure is stated by H. Kopp as follows :—

$$V_t = 1 + 0.0006744t + 0.000001721t^2 - 0.00000000050408t^3$$

The presence of small quantities of impurities such as water, naphthalene, or pyridine, materially lowers the melting-point. The red colour of ordinary commercial acid seems to be induced by the presence of minute traces of metals, particularly lead (Meyke, Ber. 16, 2513 ; cf. however, Ebell, ibid. 17, Referate 69 ; Hager, ibid. 18, Referate 114 ; Yvon, Pharm. J. Trans. 1881, 1051 ; Richardson, J. Soc. Chem. Ind. 12, 415 ; Bach, Mon. Sci. (A), 8, 508 ; Kraemer and Spilker, Ber. 1890, 648). Carbolic acid is a deliquescent substance, and in damp air forms a hydrate $(C_6H_5 \cdot OH, H_2O$, which melts at 17·2° (Allen, Analyst, 3, 319). At the same time, however, it is not very readily soluble in water, 100 parts of water dissolving 4·83 parts at 11° ; 5·36 parts at 35° ; 6·19 parts at 45° ; 7·33 parts at 58° ; 11·83 parts at 77°, ; and at 84° both liquids mix in all proportions ; whilst conversely, 100 parts of phenol dissolve 23·3 parts of water at 9° ; 26·75 parts at 32° ; 31·99 parts at 53° ; and 40·72 parts at 71° (Alexejeff, Ber. 10, 410). According to Hamberg (ibid. 4, 751), however, it dissolves in 15 parts of water at 16°–17°. It is soluble in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerol, olive oil, chloroform, carbon disulphide, &c. The aqueous solution becomes coloured violet by ferric chloride and is without action on litmus. According to Kramers, a mixture of benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, is obtained when the vapour of carbolic acid is passed through a red-hot tube (Annalen, 189, 129). Two isomeric mononitrophenols are obtained by the action of dilute nitric acid (sp.gr. 1·34) (Fritzsche, ibid. 110, 150) ; and at a lower temperature, the *para-* and at higher temperatures

the *ortho-* derivative appear to be chiefly formed (Goldstein, Ber. 11, 1943). By the further action of nitric acid, dinitrophenol (Kolbe, 4, 147, 67), and trinitrophenol (picric acid) (Schmitt and Glutz, *ibid.* 2, 52), result.

Chlorine (Laurent, Annalen, 23, 60, 43, 209 ; Faust and Muller, *ibid.* 173, 303 ; Benedikt, Monatsh. 4, 233 ; Benedikt and Schmidt, *ibid.* 4, 606) and bromine (Korner, Annalen, 137, 200, 205, 208, 209, 210 ; Hubner and Brenken, Ber. 6, 171) convert carbolic acid at the ordinary temperatures into mono-, di-, and tri-substitution derivatives, and at higher temperatures or in the presence of halogen carriers, such as antimony pentachloride, &c., into tetra- and penta- derivatives. The nitro-, chloro-, and bromo- derivatives of carbolic acid are fairly strong acids, and the acid character increases with the number of nitro- groups or chlorine or bromine atoms introduced into the molecule. Iodine yields mono- and di- derivatives in the presence of mercury (Hlasiwetz and Weselsky, Ber. 2, 524) or iodic acid (Körner, Annalen, 137, 213). Sulphuric acid converts carbolic acid into two isomeric monosulphonic acids (Kekulé, Zeitsch. f. Chem. [2] 3, 107), of which the *ortho-* acid is the chief product at the ordinary and the *para-* acid at higher temperatures. When heated with ammonium zinc chloride at 280°–300°, carbolic acid yields aniline, together with di-phenylamine and phenyl ether (Merz and Weith, Ber. 13, 1299). When fused with caustic potash, salicylic acid, metahydroxy-benzoic acid and two isomeric diphenols are formed (Barth and Schreder, *ibid.* 11, 1332), whilst fusion with caustic soda results in the formation of pyro-catechol (catechin), resorcinol (resorcin), and phloroglucol (phloroglucin) (*ibid.* 12, 417). The behaviour of sodium and potassium phenates (carbolates), when heated in a current of carbon dioxide, has been studied by Kolbe (J. pr. Chem. [2] 10, 89 ; *cf. also* Schmitt, J. pr. Chem. [2] 31, 410 ; D. R. P. 29939, June 24, 1884) ; with sodium phenate, the reaction commences below 100°, is most rapid and complete about 180°, and continues up to the temperature of the decomposition of sodium salicylate with the formation of that compound as sole product, but with potassium phenate, salicylate is formed only at temperatures below 150°, whilst at higher temperatures the isomeric potassium para-hydroxy-benzoate constitutes almost the entire product ; in these reactions, one half of the phenol is recovered. When carbolic acid is heated with phthalic anhydride and a dehydrating agent, such as zinc chloride or sulphuric acid, it yields phenolphthalein (Baeyer, Ber. 9, 1230 ; Annalen, 202, 68).

If the acid is heated with oxalic acid and sulphuric acid, it is converted into coralline (Zulkowsky, Annalen, 194, 119, 202, 184), from which pure aurine can be extracted by suitable methods (Dale and Schorlemmer, *ibid.* 196, 77), whilst benzaurine results from heating carbolic acid with benzotrichloride (Doebner-Ber. 12, 1462).

Reactions.—(1) In aqueous solution, carbolic acid gives a violet colour with ferric chloride ; this, however, is neither developed in very dilute solutions (Sarauw, Ber. 45, 46) nor in the presence of alcohol (Hesse, Annalen, 182, 161) ; limit of sensitiveness, 1 in 2000 (Polacci, Ber.

7, 360). (2) The aqueous solution, on treatment with ⅓ vol. of ammonia and then with a few drops of an aqueous solution of bleaching powder (1 part in 20 parts of water), gives either at once or on standing a blue colouration ; limit of sensitiveness, 1 in 4000 (Salkowski, Zeitsch. anal. Chem. 11, 316). (3) Bromine water, added to an aqueous solution of carbolic acid, gives either at once or on standing a yellowish-white flocculent precipitate of tribromophenol bromide (Landolt, Ber. 4, 770) ; limit of sensitiveness, 1 in 43,700 (*ibid.*), 1 in 80,000 (Lunge) (4) A solution of carbolic acid assumes a deep-red colour when boiled with one-third to one-half its bulk of Millon's reagent (a 10–15 p.c. solution of mercurous nitrate containing nitrous acid) ; limit of sensitiveness, reaction distinct with 1 in 60,000, and still appreciable with 1 in 200,000. Salicylic acid gives a similar reaction (Plugge, Zeitsch. anal. Chem. 11, 173 ; Almen, J. 1878, 1079).

Quantitative Estimation.—Carbolic acid occurs in commerce in different qualities ; as crude acid, as liquid acid, and as crystallised acid of varying degrees of purity. The percentage of phenols in crude carbolic acid can be approximately determined by shaking it with twice its volume of 10 p.c. soda ley added gradually ; the separation of the oily and aqueous layers becomes more accurate if a known quantity of petroleum spirit equal in volume to that of the layer of indifferent and resinous substances, is added, and the amount added afterwards deducted. The phenols are estimated in a portion of the aqueous layer by treatment with hydrochloric acid and subsequent addition of salt to ensure a complete separation. Such a correction is, however, hardly called for, since the phenols will dissolve about as much water as the water will dissolve phenols (Beckurts, Arch. Pharm. [3] 24, 572). Beckurts (*ibid.* [3] 24, 580) also states that Koppeschaar's method (*v. infra*) gives satisfactory results for testing liquid carbolic acid when the specimen is free from cresols. Casthelaz (Bull. Soc. Chim. 42, 574) tests measured samples of crude or liquid carbolic acid in tubes with water, with sulphuric acid (1 to 1), and with soda solution (1 part soda ley (sp. gr. 1·38) to 9 parts of water), and finally fractionates a fourth sample.

The exact quantitative estimation of carbolic acid in the pure product is always made by precipitating it with bromine. The composition of the precipitate was believed to be tribromophenol (Landolt) until it was ascertained by Benedikt that under certain conditions it was partially composed of tribromphenol bromide (*cf.* Weinreb and Bondi, Monatsh. 6, 506). Koppeschaar's method (Zeitsch. anal. Chem. 15, 233), the one usually employed, requires the following solutions ; (*a*) solution of sodium thiosulphate equivalent to a solution of iodine containing 5 p.c. of iodine ; (*b*) solution of starch ; (*c*) bromine water (titrated with pure carbolic acid), or preferably a solution of bromine in caustic soda prepared by adding an excess of bromine to the soda and subsequently removing the excess either by boiling (Allen, J. Soc. Chem. Ind. 1884, 64) or by evaporating the solution to dryness and again dissolving in water ; (*d*) solution of potassium iodide containing 125 grams in the litre. The process consists in treating 25 c.c.

of the aqueous solution of carbolic acid (4 grams in the litre) with 100 c.c. either of the solution of bromate and bromide with 5 c.c. of concentrated hydrochloric acid to liberate the bromine, or of bromine water in a stoppered bottle, which is then well shaken, allowed to remain for 15 minutes, treated with 10 c.c. of potassium iodide solution, again shaken, and titrated with thio-sulphate. The reactions involved are the following :—
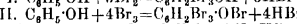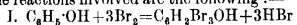
I. $C_6H_5 \cdot OH + 3Br_2 = C_6H_2Br_3OH + 3HBr$
II. $C_6H_5 \cdot OH + 4Br_2 = C_6H_2Br_3 \cdot OBr + 4HBr$
III. $C_6H_2Br_3 \cdot OBr + 2KI = C_6H_2Br_3 \cdot OK + KBr + I_2$

(Weinreb and Bondi, l.c.) ; so that, as Beckurts points out (l.c. infra), the assumption made by Koppeschaar in the preceding method, that 6 atom. props. of bromine enter into combination with 1 mol prop. of phenol, is in practice correct. Beckurts (Arch. Pharm. [3] 24, 562) gives the following as the best mode of estimating carbolic acid : The solutions employed are (a) 1120 normal potassium bromide (5·939 grams in the litre) ; (b) centinormal potassium bromate (1·666 grams in the litre) ; (c) potassium iodide solution containing 125 grams in the litre ; (d) decinormal sodium thiosulphate (24·8 grams of $Na_2S_2O_3,5H_2O$ in the litre). For the titration, 25 to 30 c.c. of the phenol solution (1 in 1000) are treated with 50 c.c. each of the potassium bromate and bromide solutions, shaken with 5 c.c. of concentrated sulphuric acid, allowed to remain 15 minutes, treated with 10 c.c. of the potassium iodide solution, and finally titrated with thiosulphate to estimate the amount of iodine liberated. The calculation is simple : from the 50 c.c. each of bromate and bromide solution, 0·2397 gram of bromide is liberated by the sulphuric acid, and this is capable of converting 0·0469 gram of carbolic acid into tribromophenol ; 1 c.c. of the decinormal thiosulphate is equivalent to 0·008 gram of bromine, a quantity capable of converting 0·00156 gram carbolic acid into tribromophenol ; multiplying now 0·00156 by the number of c.c. of thiosulphate used, and subtracting the product from 0·0469, gives the weight in grams of phenol in the quantity of solution originally taken. This process is accurate whenever solutions of pure carbolic acid, or mixtures from which the pure acid can be separated, are to be tested, but it fails in all cases (e.g. crude carbolic acid) when other phenols, particularly cresols, are also present. Methods for the estimation of carbolic acid have also been proposed by Waller (Chem. News, 43, 152), Degener (J. pr. Chem. [2] 17, 390), and Chandelon (J. Soc. Chem. Ind 1882, 203) ; but these are inaccurate (Beckurts). Other methods have been proposed by Moerk (Chem. Zentr 1904, ii. 1764) ; Messinger and Vortmann (Ber. 1890, 2753) ; Schryver (J. Soc. Chem. Ind. 1899, 553) ; Weiss and Downs (J. Ind. Eng. Chem. 1917, 9, 569) ; Fox and Barker (J. Soc. Chem. Ind. 1917, 36, 842 ; idem. 1918, 265 T.) ; and Petrie (idem. 1919, 132 T.). A biological method for the determination of phenol has been proposed by Blyth and Goodban (J. Soc. Chem. Ind. 1907, 632), and an iodometric method by Skirrow (ibid. 1908, 58) ; and Wake and Inglis have investigated the iodine values of the phenols (ibid. 1908, 315). A method has been devised by Allen for determining phenols in carbolic soap (Analyst, 1886, 103).

Uses.—Carbolic acid has powerful antiseptic properties and is used on the large scale as a disinfectant. Large quantities of carbolic acid are also employed in the manufacture of salicylic acid ; whilst in the colour industry, a considerable demand for the acid exists, inasmuch as it is the source of picric acid and coralline, and it is used in the preparation of some azo- colours. Phenol has, of late years, been very largely used for the preparation of modern high explosives. ' Lyddite ' and ' melinite,' consisting very largely of picric acid and picrates, although trinitrotoluene appears now to be replacing picric acid. Phenol forms condensation products with formaldehyde which are bodies of resinous appearance and properties, and which are proposed as substitutes for natural gums and shellac.

Compounds with Metals.—Potassium phenate $C_6H_5 \cdot OK$, formed by dissolving potassium in carbolic acid (Hartmann, J. pr. Chem. [2] 16, 36), or by heating carbolic acid with caustic potash (Baumann, Ber. 10, 686), crystallises in slender white needles, readily soluble in water, alcohol, and ether. Sodium phenate can be prepared by similar methods and may be used in the manufacture of salicylic acid and as a disinfectant. Compounds with barium (Laurent) and lead (Calvert, Zeitsch. Chem. 1865, 531) have also been described.   W. H. C.

CARBOLINEUM. A preparation of crude carbolic acid. Used as an antiseptic and preservative.

CARBON. Sym. C. At. wt. 12. Carbon boils at 3600° (Violle, Compt. rend. 1892, 115, 1273 ; 1895, 120, 868). Carbon occurs in nature in the free state, and very abundantly in combination, notably in the form of carbonates, and as an essential constituent of organic bodies. In the free state it is a solid, without taste or smell, exhibiting great diversity in the physical characteristics of its three allotropic forms—diamond, graphite, and charcoal.

The diamond, up to the time of Bergman, was supposed to be a kind of rock-crystal, although Newton regarded it as probably an unctuous substance coagulated. It was shown to be combustible by the members of the Academy del Cimento in 1694, and Lavoisier proved that the sole product of its combustion was carbon dioxide. He had previously ascertained that this gas was a compound of oxygen and an element to which he gave the name of carbone, contained in coal and wood. Graphite, as its synonyms, blacklead and plumbago (from the Italian grafio piombino—the writing lead), imply, was long considered to be a kind of lead, or as related to antimony ; Scheele regarded it as a compound of iron and carbon ; Kastner proved that it was essentially carbon. Carbon combines directly with hydrogen at 1100°–1200°, forming hydrocarbons (Bone and Jerdan, Chem. Soc. Proc. 1901, 162 ; Bone and Coward, ibid. Trans. 1908, 1975 ; 1910, 1219 ; Proc. 1908, 222 ; Pring and Hutton, Trans. 1906, 1591 ; Pring, ibid. 1910, 498). At high temperatures, such as the electric furnace, it is dissolved by the alkaline earth carbides and by rhodium, iridium, palladium, and platinum (Kahn, Compt. rend. 1906, 143, 49 ; 1907, 144, 197 ; Moissan, ibid. 122, 1479). At the temperature of the electric arc, carbon reduces alumina (Moissan, ibid. 1894, 119, 935).

Manufacture of Wood Charcoal.—The earliest plan of *coaling wood*, as the manufacture of charcoal was termed and is still called, is carried on as follows : A piece of ground is levelled at some convenient spot in the forest, which is termed the 'hearth' or 'earth.' In the centre of this a thick pole or bundle of brush-wood is placed, around which the wood is arranged, some of the pieces being laid horizontally and others set up at an inclination, or the wood may be placed altogether at any steep angle, sloping outwards from the centre to form a flattened cone, which, when complete, is usually called a heap ; the object, whichever way the wood is placed, is to obtain a free circulation of air under the heap to communicate with the chimney in the centre, which is formed by then withdrawing the centre pole or bundle of brushwood. The large wood should, if convenient, be at the bottom of the heap, and the outside packed as close as possible , the heap is then covered with small brushwood, and afterwards with turf, or the material most impervious to air which can be conveniently obtained. A fire is lighted in the centre chimney, and by leaving openings in the outside covering at the bottom of the heap, the fire soon extends, and can be guided to any part by making temporary openings to admit the air. When the heap is sufficiently fired, all the openings are closed, and lastly the chimney itself. The fire will always extend most rapidly on the side facing or towards the wind, and great care must be taken to watch and check this, by keeping the covering on that side in good order. The charcoal burner must always be careful to spread the fire as evenly as possible through the heap, and after it is coaled to stop it down carefully ; he can always accelerate the process in any part of the heap, if well built, by opening the outside to admit air freely, but if he finds this does not act, from any fault in setting the wood, he had better open a hole with a bar at the place required, and light a fire in the hole ; this will soon communicate with the main fire in the heap. As soon as the smoke and white flame cease to escape at the vents, the whole heap must be closed from the air as carefully as possible until the charcoal is quite cooled, and is ready to draw. The fire must never burn too fast ; the slower the process, if the fire is steady and regular, the better the yield of charcoal. Hard close-grained woods take a longer time to coal than soft open-grained woods, and should be placed in the heap accordingly. These technical instructions, handed down in the forests for ages as secrets from father to son amongst the 'coalliers' in every country in Europe, are the results of long practical experience, and strictly accord with the true principles on which the process is based.

To carbonise wood under a movable covering, the plan of *meiler*, or heaps, is employed in Germany. The wood is arranged either in horizontal layers or in nearly vertical ones with a slight slope, so as to form conical rounded heaps of different sizes. The former are called 'lying *meiler* ' (Fig. 1) ; the latter, 'standing *meiler* ' (Figs. 2 and 3). Both are distributed in much the same way.
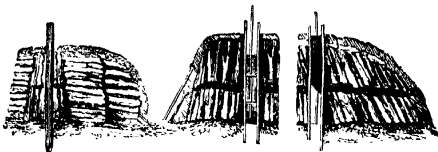
FIG. 1.   FIG 2.   FIG. 3.

In districts where the wood can be transported by means of rivers or mountain slides, a dry flat space must be pitched upon (screened from storms and floods), which may be walled round, having a slight declivity made in the ground towards the centre (*v.* Fig. 4). Into this space the tarry acid will partially fall, and may be conducted outwards through a covered gutter beneath into a covered tank. The mouth of the tank must be shut during the coking with an iron or stone slab, luted with clay. A square iron plate is placed over the inner orifice of the gutter to prevent it being choked with coal ashes.

Fig. 4 represents a walled *meiler* station : *a*, the station ; *b*, the gutter ; *c*, the tank, which is covered with the slab *d* ; *e*, a slab which serves to keep the gutter clear of coals. The cover of the heaps is formed of earth, sand,

FIG. 4.

ashes, or such other matter as may be most readily found in the woods. They should be kindled in the centre. From 6 days to 4 weeks may be required for charring a heap, according to its size, hard wood requiring more time, and the slower the process the better and greater is the product, generally speaking.

Charring of wood in mounds (*haufe* or *liegende werke*) (Figs. 5 and 6) differs from that in the *meiler*, because the wood in the *haufe* is successively charred, and the charcoal
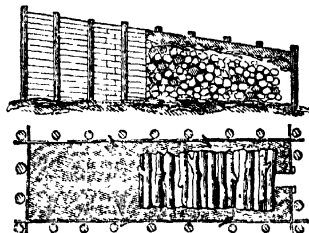
FIGS. 5 and 6.

is raked out little by little. The product is said to be greater in this way, and also better. Uncleft billets, 6 or 8 feet long, being laid over each other, are covered with ashes, and then

carbonised. The station is sometimes horizontal and sometimes made to slope. The length may be 24 feet, the breadth 8 feet, and the wood is laid crosswise. Piles are set perpendicularly to support a round made of boughs and leaves covered with ashes. Pipes are occasionally laid within the upper parts of the mounds, which serve to catch and carry off some of the liquid.

Fig. 7 is a vertical section, and Fig. 8 a half bird's-eye view and half cross-section at the
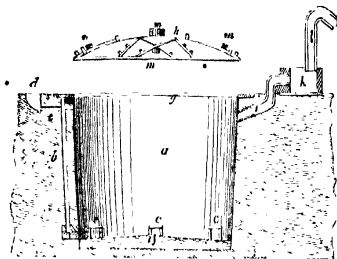
FIG. 7.

height of the pit bottom, of Chabeaussière's kiln for making wood charcoal. *a* is the oven ; *b*, vertical air-pipes ; *c, c,* horizontal flues for admitting air to the kilns ; *d, d,* small pits which communicate by short horizontal pipes, *e, e,* with the vertical ones ; *f,* the sole of the kiln, a circle of brickwork upon which the cover or hood *h* reposes ; *i,* a pipe which leads to the cistern *k* ;
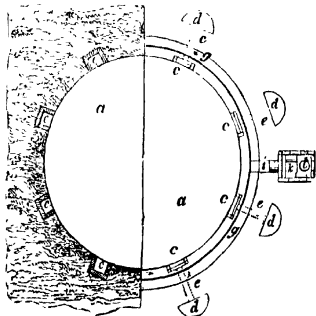
FIG. 8.

l, the pipe destined for carrying off the gaseous matter ; *m, m,* holes in the iron cover or lid.

The distribution of the wood is like that in the horizontal *meiler* or heaps ; it is kindled in the central vertical canal with burning fuel, and the lid is covered with a few inches of earth. At the beginning of the operation all the draught flues are left open, but they are progressively closed as occasion requires. In 8 kilns of this kind 500 decasters of oak wood are carbonised, from which 15,000 hectolitres of charcoal are obtained, equal to 64,000 lbs. French, being about 25 p.c., besides tar and 3000 velts of wood vinegar of from 2° to 3° Baumé.

At Crouy-upon-the-Ourcq, near Meaux, there is a well-constructed kiln for making turf-charcoal. It resembles most nearly a tar kiln. In Fig. 9, *a* is the cylindrical coking place whose surrounding walls are heated by the flame which passes through the intermediate space *b*. The place itself is divided by partitions of fire tiles into three stages, through the apertures in which the flames of the fire, *c, c,* rise, and heat the exterior of the coking apartment. In order to confine the heat, there is in the enclosing walls of the outer kiln a cylindrical hollow space, *d,* where the air is kept stagnant. Through the apertures left in the upper end at *e,* the turf is introduced ; they are then shut with an iron plate, *f,* which is covered with ashes or sand. The fireplace opens above this aperture, and its outlet is provided with a movable iron cover, *g,* in which there is a small hole for the issue of the gases. The sole of the kiln consists of a cast-iron slab, *h,* which may be raised by means of a hook, *i,* upon it. This is drawn back after the carbonisation is completed, whereby the charcoal falls from the coking space into a
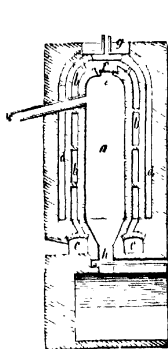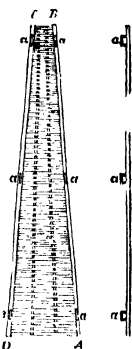
FIG. 9. FIG. 10. FIG. 11.

subjacent vault. The volatile products are carried off by the pipe *k,* and led into the condensing cistern, the gases escaping to the fireplace, where they are burned. The iron slab is protected from the corrosion of the acid vapours by a layer of coal ashes.

Charcoal obtained by the action of a rapid fire in close vessels is not so solid and so good a fuel as that which is made in the ancient way by the slow calcination of pyramidal piles covered with earth. According to Juon (Stahl and Eisen, 1904, 24, 1230), this is due merely to the difference in temperature of the two processes, the higher temperature used in the heapmade carbon increasing the carbon content. One of the most economical ovens for making wood charcoal is that invented by M. Foucauld, which he calls a shroud or *abri.* To construct one of those, 30 feet in diameter at the base, 10 feet at its summit, and from 8 to 9 feet high, he forms, with wood 2 inches square, a frame 12 feet long, 3 feet broad at one end, and 1 foot at the other end.

The Figs. 10 and 11 will explain the

construction. The uprights, A, B, and C, D, of this
frame are furnished with three pairs of wooden
handles, a, a, a, by means of which they can be
joined together, by passing through two con-
tiguous handles a wooden fork, the frame being
previously provided with props, as shown in
Fig. 11, and covered with loam mixed with
grass. A flat cover of 10 feet diameter, made
of planks well joined, and secured by four cross-
bars, is mounted with two trap doors, M, N
(Fig. 12), for giving egress to the smoke at the
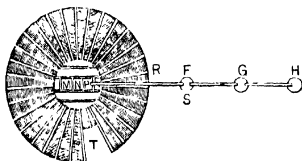
FIG. 12.

commencement of the operation ; a triangular
hole, P, cut out in the cover, receives the end of
the conduit, Q, R, S (Figs 12 and 13), of wood
formed of three deals destined to convey the
gases and condensed liquids into the casks F, G, H.
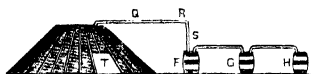
FIG. 13.

Lastly, a door, T, which may be opened and shut
at pleasure, permits the operator to inspect the
state of the fire. The charcoal calcined by this
abri has been found of superior quality.

When it is wished to change the place where
the abri is erected, and to transport it to a store
of new-felled timber, the frame is taken down,
after beating off the clay which covers it ; the
joints are then cut by a saw, as well as the ends
of the fork which fixed the frames to one
another. This process is economical in use and
simple and cheap in construction, since all the
pieces of the apparatus are easily moved about,
and may be readily mounted in the forests. For
obtaining a compact charcoal for the use of
artisans, this mixed process of Foucauld is said
to be preferable to either the close iron cylinder
or the pile.

The fierce process for the production of
charcoal, in which the wood is heated in brick
kilns shaped like a bee-hive, of 32 feet diameter
and 16 feet high in the centre, by means of the
combustion of the permanent gases produced
during a previous process, is said to produce a
far higher percentage of charcoal and to involve
a smaller loss of by-products (Dudley, J. Anal.
and Appl. Chem. May, 1891 ; Armour, Bowers,
J. Soc. Chem. Ind. 1892, 152).

The charcoal made at Ontario from the
local wood is of excellent quality for blast-
furnace use. The wood is here heated in half-
iron cylinder retorts, set horizontally and about
9 feet long and 4 feet high. The retorts are
charged once a day, and are heated underneath
by the tar produced mixed with the waste from
the charcoal. The distillate is condensed by

straight condensers, one of which is attached to
each retort (Goodwin, J. Soc. Chem. Ind. 1902,
743).

In other processes wood is carbonised by
superheated steam (Elfeström, Proc. Inst. Civil
Eng. 1906, 164, 60 ; Zwilbger, J. Soc. Chem. Ind.
1891, 129).

According to Rubands (J. Soc. Chem. Ind.
1902, 1466), a hygienic and antiseptic wood
charcoal is obtained by heating a mixture of
aromatic plants, such as juniper, thyme, broom,
&c., in an oven until the cresols begin to come
off. The mass is then thrown into sheet-iron
boxes, sealed to prevent combustion, and allowed
to cool, the empyreumatic matters thus being
reabsorbed.

A large number of improvements in the
apparatus employed for obtaining wood char-
coal have been proposed (Jones, Eng. Pat.
1485, 1894 ; J. Soc. Chem. Ind. 1895, 24 ; Wise
Waworth, Eng. Pat. 10522, 1897 ; ibid. 1899,
128 ; Schenk, Eng. Pat. 23085 ; ibid. 1900, 321 ;
Burcy, ibid. 1902, 909 ; Mourlot, ibid. 1902,
1448 ; Blacher, Chem. Ind. 23, 508).

Charcoal is also prepared from sawdust,
wood, chips, and peat. The raw material is
fed and pressed into and through heated retorts
in a continuous stream, and comes out at the
other end of the furnace as hard charcoal. The
retorts are provided with pipes for drawing off
the by-products (Heidonstam, J. Soc. Chem. Ind.
1898, 445). Many other methods of converting
peat into charcoal have been described (Rose,
ibid. 1896, 643 ; Eng. Pat. 17568, 1895 ;
Calmont, ibid. 1892, 257 ; Eng. Pat. 3978 ;
Zohrab, ibid. 1893, 437 ; 1897, 1006 ; Eng.
Pat. 3619, 1892 , Jurgensen and Bauschlicker,
Chem. Zeit. 1901, 25, 635 ; Stauber, J. Soc.
Chem. Ind. 1906, 685 ; Jürgensen, ibid. 1907,
685).

For blast-furnace work, peat charcoal and
that obtained from birchwood is the best.

According to Maubér (ibid. 1890, 881),
charcoal is also produced from the by-products
in the manufacture of spirits from grains and
cereals. Charcoal suitable for use as filters,
respirators, and as wick for candles, can be
prepared by placing vegetable fibres, such as
cotton, cotton fabric or waste threads into
drums, which are placed one by one into an
inclined furnace, down which they roll to the
lower end, which is provided with an exit door.
When no more gases are given off, the drums are
withdrawn and the charcoal washed with water
(Cooper, J. Soc. Chem. Ind. 1902, 421).

For making gunpowder charcoal the lighter
woods, such as the willow, dogwood, and alder,
answer best ; and in their carbonisation care
should be taken to let the vapours freely escape,
especially towards the end of the operation, for
when they are reabsorbed, they greatly impair
the combustibility of the charcoal (Taylor and
Challon, ibid. 1890, 106.

The charcoal of some woods contains silica,
and is therefore used for polishing metals.
Being a bad conductor of heat, charcoal is
employed sometimes in powder to encase small
furnaces and steam-pipes. It is not affected by
water, and hence the extremities of stakes
driven into moist ground are not liable to de-
composition. In like manner casks when charred
inside preserve water much better than common

casks, because they furnish no soluble matter for fermentation or for food to animalcules.

For making crayons of charcoal the willow is the best wood that can be employed, as the softness is uniform in all its parts. The durability of charcoal may be seen in several of our old churchyards, where the letters made with lampblack are still perfect, though the white lead with which the body of the stones was painted is entirely destroyed. This property of carbon is shown, however, in a more striking manner by the writings that were found in the ruins of Herculaneum, which have retained their original blackness for two thousand years. The ancients wrote with ink made from ground charcoal.

If it be required to purify any carbonaceous matter to render it fitter for delicate pigments, this may be done by first calcining it in a close vessel, and then lixiviating it in water slightly acidulated by nitric acid.

The incorruptibility of charcoal was well known to the ancients, and they availed themselves of this property upon all important occasions.

Some years ago a quantity of oak stakes were found in the bed of the Thames, in the very spot where Tacitus says that the Britons fixed a vast number of such stakes to prevent the passage of Julius Cæsar and his army. These stakes were charred to a considerable depth, had retained their form completely, and were firm at the heart.

Desmond found that wood charcoal, when submitted to a high temperature out of contact with air, evolved a considerable quantity of gas consisting of 9·14 p.c. CO_2, 18·08 p.c. CO, 49·11 p.c. H_2, 16·04 p.c. CH_4, 0·26 p.c. O_2, and 7·37 p.c. N_2, its antiseptic properties being superior to carbon monoxide (Compt. rend. 1894, 119, 733).

Most of the houses in Venice stand upon piles of wood, which have all been previously charred for their preservation. In this country estates were formerly marked out by charred stakes driven to a considerable depth into the ground. These are occasionally found, and usually the charred portions are quite perfect, although every other part is decayed (v. Wood, DESTRUCTIVE DISTILLATION OF).

Wood charcoal possesses in a remarkable degree the power of absorbing gases in its pores, and in many cases of determining their combination. This power increases with its density. As ordinary charcoal contains atmospheric air in its pores, it must for this purpose be prepared by heating it to redness in a close vessel, and cooling over mercury. The following table shows the absorptive power of Saussure boxwood charcoal of sp. gr. 157 for different gases :—

Ammonia gas	.	.	90 vols.
Hydrochloric acid gas		.	85 ,,
Sulphur dioxide		.	65 ,,
Hydrosulphuric acid	.		55 ,,
Nitrous oxide	.	.	40 ,,
Carbon dioxide	.		35 ,,
Ethylene	.		35 ,,
Carbon monoxide	.		9·42 vols.
Oxygen	.	.	9·25 ,,
Nitrogen	.	.	6·5 ,,
Hydrogen	.	.	1·25 ,,

Charcoal obtained from the shell of the cocoa-nut has still greater absorptive properties, absorbing, according to Hunter,

Ammonia	.	.	171·7 vols.
Carbon dioxide	.	.	67·7 ,,
Carbon monoxide	.	.	21·2 ,,
Oxygen	.	.	17·9 ,,

In consequence of this absorption of gases in the pores of charcoal, their chemical activity is greatly increased. When a piece of charcoal which has absorbed a considerable quantity of sulphuretted hydrogen is introduced into oxygen, a violent reaction immediately takes place, water and sulphur dioxide being set free. If air be employed instead of oxygen, sulphur is deposited.

This property is utilised in the removal of fœtid and bad-smelling gases from rooms, and in the sweetening of bad-smelling liquids and of clothes. For this purpose charcoal of average porosity is found to be the most efficient, and it should be in moderate-sized pieces, its absorbent power being greater in this state than when in fine powder or in very large pieces.

Potassium and sodium alloy absorbs charcoal, and the suspension so obtained has a variety of uses, and constitutes an intermediate product in a variety of processes such as the production of potassium cyanide and so forth (Weintraub, J. Soc. Chem. Ind. 1909, 794).

When charcoal is boiled in a solution of platinum tetrachloride, it becomes impregnated with platinum, and is known as platinised charcoal. This substance possesses in a greatly increased degree the power of inducing chemical combination.

Charcoal containing 2 p.c. of platinum causes oxygen and hydrogen to unite completely in about a quarter of an hour, the rapidity increasing with the percentage of platinum, charcoal containing a larger quantity of platinum acting like platinum sponge. Platinised charcoal may be applied to the preparation of air-filters and respirators, and also as a mild caustic (Stenhouse, Chem. Soc. Trans. 8, 105).

Charcoal is readily oxidised by dilute aqueous solutions of calcium hypochlorite, and potassium chlorate, especially in presence of osmium tetroxide, forming carbon dioxide, carbon monoxide, mellogen, and mellitic acid.

A further property of charcoal is its power of depriving most coloured liquids of their colouring matters, by absorbing them within its pores. The colouring of red wine, cochineal, madder, or indigo, can thus be removed from solutions.

This property was discovered in 1790 by Lowitz, and is made use of on the large scale in several industrial operations, particularly in the process of refining sugar. It is most strikingly possessed by bone-black or animal charcoal (q.v.). Charcoal of great decolourising power can be obtained by the dry distillation of birchwood or other substances containing carbon mixed with calcium or magnesium chloride, without access of air. The charcoal so obtained is washed with water, then with hydrochloric acid, and then again with water (Ostrejho, J. Soc. Chem. Ind. 1900, 1099 ; 1902, 58).

Charcoal of higher decolourising power is obtained from blood, horns, hoofs, clippings of hides, glue, &c., in contact with pearl-ash. A good decolourising charcoal is also obtained by

carbonising vegetable matters mixed with chalk, calcined flints, or other earthy substances.

According to Halse (J. Soc. Chem. Ind. 1903, 504), charcoal, especially applicable for use in decolourising and purifying saccharine and other liquids, and which can be used in acid solutions, is obtained by heating wood or a similar material with sulphuric acid to a temperature not exceeding 200°. The charred mass is then washed and dried, and, when spent, it can be revivified by treatment with a smaller amount of sulphuric acid.

Charcoal also precipitates or absorbs certain substances from solution, notably iodine, lime, and its salts (being used for the purification of highly calcareous waters), lead salts and most metallic subsalts, besides many organic substances, as the bitter principles of hop, gentian, and aloe, tannin, alkaloids and resins, from their alcoholic solution (de Coninck, Compt. rend. 130, 1627 ; Laval, Pharm. J. 1900, 65, 213 ; Malmegac, J. Pharm. Chim. 1900, 12, 5 ; Davis, Chem. Soc. Trans. 1907, 1666).

Crude alcohol is occasionally allowed to remain for some time in contact with charcoal.

Carbon is used for the reduction of metals from their ores, and in the manufacture of glass for the reduction of alkaline sulphates.

Porous carbon can also be used with advantage in electrolytic cells (Lob. Zeit. f. Elect. Chem. 1896, 3, 185). When used as an anode in strong hot sulphuric and other acids, which give off oxygen at the anode, carbon is dissolved, and this property can be used for depositing carbon on suitable cathodes (Coehn, J. Soc. Chem. Ind. 1897, 445).

(For the treatment of carbon articles before use, compare Thomson Houston, ibid. 1905, 1230 ; Eng. Pat. 28062, 1904 ; Acheson, U.S. Pat. 74918, 1904.)

Gas-carbon (*Glance coal*) is a very dense form of carbon, deposited in the upper part of the retorts in the manufacture of coal gas and in blast furnaces. It often exhibits the lustre and sonority of a metal, is very hard, and a good conductor of heat and electricity. It is used to form the negative element in a Bunsen battery.

Materials used for manufacture of carbon electrodes are coke, hard and soft pitch, coal tar, and petroleum oil ; in some cases, to obtain electrodes of better mechanical wearing power, a small portion of the coke is replaced by soot. The proportions of the various substances depend on the kind of electrode required. Roush (J. Ind. Eng. Chem. 1909, 1, 286 ; Lake, J. Soc. Chem. Ind. 1900, 1001 ; Cooper, Shrewsbury and Marshall, ibid. 1896, 25 ; Starts, ibid. 1906, 544 ; U.S. Pat. 819606, 1906).

According to Niewerth (J. Soc. Chem. Ind. 1894, 1206), carbons of less resistance and greater illuminating power when used in arc lamps, can be obtained by mixing the carbon with aluminous earths, magnesia, or other metalliferous minerals before moulding, after which process it is heated by means of an electric current, The carbon, when being heated, is supported in a holding sleeve of non-conducting material to prevent warping. Castner (J. Soc. Chem. Ind. 1894, 1067 ; Acheson, ibid. 1894, 407) adds 10 p.c. carbide of silicon to the carbon used for arc lamps; Rivers (ibid. 1906, 483 ; Kuffrath, ibid. 1907, 309) adds yttrium salts. Langville (ibid. 1692,

935) descr.... . ..., carbon for electrical purposes from paper pulp (Eng. Pat. 13847, 1892).

Carbon filaments are also prepared for use in incandescent lamps and electric lamps (Thomson Houston, J. Soc. Chem. Ind. 1905, 62 ; Pring and Fielding, Chem. Soc. Trans. 1909, 1497 ; Chateler and Wolagdine, Compt. rend. 1909, 148, 1715 ; Howell, Electrician, 1905, 55, 588 ; Levis, J. Soc. Chem. Ind. 1905, 721, 882 ; Eng. Pat. 6959, 1904).

Graphite is formed in the manufacture of carborundum (*q.v.*), and its production on a commercial scale has been established by Acheson (U.S. Pat. 568523). It is used to form lamp carbons, crucibles, electrodes, &c. For the lower qualities of graphite articles anthracite may be employed ; for the finer kinds, and for the manufacture of lubricating graphite, petroleum coke mixed with a catalytic oxide is used. For a discussion of the properties, mode of formation, and structure of graphitic carbon, v. Kohlschutter, Zeitsch. anorg. Chem. 1919, 105, 35.

Lampblack is prepared on the large scale by burning fat, oil, resin, tar, &c., with an imperfect supply of air, either in a brick furnace or in cast-iron chambers.

The resulting dense black smoke is conducted into large chambers, where, on account of the extremely sluggish draught, it is allowed to roll about until the particles gradually coalesce into masses which after some time fall on the floor as soot. The condensation of the particles may be greatly facilitated by sending a current of electricity through the atmosphere of smoke, or else it can be agitated by mechanical means (Irvine, J. Soc. Chem. Ind 1890, 1110).

For an account of the history and development of the lampblack and carbon-black industry, see Cabot, 8th Int. Cong. Appl. Chem. 1912, Ve, 12, 13.

When commercial lampblack is strongly heated, a large amount of empyreumatic matter is given off, which condenses into a brown greasy mass consisting of chrysene, pyrene, capnomar, &c. This causes ordinary lampblack to cohere when pressed. After calcination it loses this property.

Creosote or other suitable carbonaceous fuel is burnt in a furnace with an adjustable air supply, and the products of combustion are sent through a cooler, where by-products are condensed in centrifugal separators, the carbon, deposited being collected in underlying receivers (Adam, J. Soc. Chem. Ind. 1907, 701 ; Eng. Pat. 13301, 1906).

An arrangement of lamps for the preparation of an especially fine quality of lampblack from waste fat and mineral oils is described in Payen-Paul, 64, 65.

Numerous improvements in the apparatus for the production of lampblack have been described (Wegelin, J. Soc. Chem. Ind. 1898, 747 ; 1899, 925 ; 1900, 56 ; 1902 1622 ; 1903, 1190 ; 1908, 81, 579 ; Fr. Pat. 380983, 1907 ; Irvine, J. Soc. Chem. Ind. 1890, 1110 ; Sanders, ibid. 1800, 753 ; Lembdner, ibid. 1903, 1238 ; U.S. Pat. 741726, 1903 ; Smith, J. Soc. Chem. Ind. 1909, 430 ; Meiser, ibid. 1908, 1212 ; D. R. P. 203711 ; Lennard, J. Soc. Chem. Ind. 1899, 1009 ; Ogilvy, ibid. 1902, 1084).

*Carbon has also been obtained direct from smoke (Ward, *ibid.* 1897, 902). Irvine (*ibid.* 1894, 532) obtains lampblack by spraying tars or oils rich in carbon over incandescent coke, mixing the gases so produced with air and steam, and burning them with a limited supply of air.

Lampblack, carbon black, also sometimes spoken of as gasblack, hydrocarbon black, jet-black, and so forth, is used in the production of printer's ink, paints, mineral-black, stove polish, shoe leather, rubber goods, fertilisers, colouring cement, mortar pulp, and artificial stone, harness oil, stencilling, &c. It varies in composition and properties with the material and method used in its production.* When produced from the natural gas in American oil wells, the carbon-black differs from ordinary lampblack, by mixing with water on being shaken with it ; ordinary lampblack will not do this. It is also quite different in appearance from lampblack obtained from oils, having a fine velvet-like gloss

(*See* description of figure and apparatus for manufacture, Cabot, J Soc. Chem Ind 1894. 130. *Cf.* also Purtle and Rowlands, *ibid.* 1908, 234 ; U S. Pat. 877596, 1908 ; Prosch, J. Soc Chem Ind. 1903, 640 ; Buller, Min and Eng. World, Oct 28, 1911)

A good lampblack, said to be superior to the best American blacks, is also obtained by sparking a mixture of hydrocarbons under pressure and with or without admixture of carbon di- or mon-oxide (Koppers, J. Soc. Chem. Ind. 1906, 13 ; Machtolf, *ibid.* 894, 1909 ; 482, 1050 ; D. R. P 207520, 1907 ; Gollwert, J Soc. Chem. Ind. 1909, 1050). According to Frank (*ibid.* 1900, 545 ; 1905, 29, 1044), the carbon, at the moment of liberation, is readily taken up by metals ; it can thus be made to pass into silver, imparting to the latter the appearance of so-called oxidised silver.

According to Peters, lampblack suitable for use in the preparation of paints, can also be obtained by heating the waste carbons from arc lamps to 1200°–1400°, and then allowing the mass to cool slowly (*see* also *Acetylene black*).

Colloidal carbon. By the careful addition of sugar to concentrated sulphuric acid, filtering and dialysing the liquid, a clear black stable solution of colloidal carbon may be obtained (Sabbatani, Kolloid-Zeitsch. 1914, 14, 29).

Carbon monoxide ; *carbonous* or *carbonic oxide* ; *formic anhydride* CO ; sp.gr. 0·96716 (Rayleigh), 0·96702 (Leduc) (air = 1). V.D. 14. (−186°) (Wroblewski, Compt. rend. 98, 982). S.H.p. 0·2346. S.H.v. 0·16844 (Wiedemann, Pogg. Ann. 157, 1). C.E. 0·003667 (Regnault). S. (6°) 0·0287 ; (9°) 0·0269 ; (18·5°) ; 0·02315 (Bunsen). S. alcohol (2°) 0·20356 ; (13°) 0·20416 ; (16°) 0·20566 ; (24°) 0·20452 (Bunsen) ; $\mu_c = 1·000301$; $\mu_R = 1·00035$; $\mu_v = 1·000391$ (Croullebois, Ann. Chim. Phys. [4] 20, 136). Does not exactly obey Boyle's law ; $PV/P_1V_1 = 1·00293$ (Regnault). Its critical temperature is −138·7±0·1, and the corresponding pressure 34·6±1 atmospheres, critical density 0·3110. It boils at −190°.

Discovered by Lassonne, and independently by Priestley. Composition first established by Clement and Desormes. *

Carbon monoxide is present in coal- and water-gas, from both of which it is sometimes obtained industrially (Williams, J. Soc. Chem. Ind. 1891, 270 ; Claus, *ibid.* 1890, 170).

Produced by the oxidation of charcoal at high temperatures (*cf.* Johnson and McIntosh, Trans. Roy. Soc. Canada, 1913, 7, iii. 161). By the reduction of carbon dioxide by means of hydrogen, carbon, metals, &c., at a red heat, or over carbon made incandescent electrically and coated with a bad conducting material (Engels, J. Soc. Chem. Ind. 1901, 350). On the rate of reduction of carbon dioxide by carbon, *see* Rhead and Wheeler (Chem. Soc. Trans. 1912, 101, 831, which contains a number of references to previous work on the subject). In the reduction of metallic oxides by charcoal or coke. By the dry distillation of many organic compounds, and together with hydrogen and carbon dioxide when steam is passed over red-hot charcoal. By passing electric sparks through carbon dioxide (Buff and Hofmann, Annalen, 113, 140) or by heating carbon dioxide to 1300° (Deville, Compt. rend. 59, 873). By heating dehydrated oxalic acid, or by heating dry alkaline formates and acetates with formic acid (Lorm, *ibid.* 82, 750). By heating an oxalate or formate or these acids with concentrated sulphuric acid.

Carbon monoxide is also produced in considerable quantities from various explosives, such as melinite, gun cotton, &c. It is evolved by an alkaline pyrogallol solution during the absorption of oxygen, unless a large excess of potash is employed (Clowes, Chem. Soc. Proc. 1895, 200).

Prepared by the decomposition of (1) oxalic or formic acid, (2) potassium ferrocyanide, or (3) potassium cyanide, by concentrated sulphuric acid (Boudouard, Compt. rend. 1899, 128, 98, 307, 822 ; Wade and Panting, Chem. Soc. Trans. 1898, 257).

(1) $C_2H_2O_4 = CO + CO_2 + H_2O$
(2) $CH_2O_2 = CO + H_2O$
(3) $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O$
$\quad = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4$

In the first case the gas is mixed with carbon dioxide, which must be removed by passing through potash or lime-water. In the last reaction it is free from carbon dioxide if the temperature does not exceed 200°, but above this point this gas and sulphur dioxide are produced by the reducing action of carbon monoxide upon sulphuric acid :

$$H_2SO_4 + CO = CO_2 + SO_2 + H_2O$$
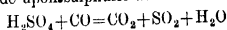
It is liable also to contain a small quantity of hydrocyanic acid vapour.

Dry calcium oxalate or barium oxalate is mixed with about $\frac{1}{10}$ dry lime, and strongly heated, the gas passed through lime and dried : $CaC_2O_4 = CaCO_3 + CO$, any carbon dioxide formed being absorbed by the lime. Carbon monoxide is evolved in the manufacture of carbides, and is collected and stored. It is also produced in the decomposition of sugars.

Carbon monoxide is manufactured practically pure by bringing a mixture of oxygen and carbon dioxide in contact with incandescent graphite, coke, anthracite, &c. As thus obtained, it may be used for the manufacture of special steels, the reduction of refractory oxides, the treatment of iron ores in the blast furnace, and for other

purposes (Loiseau, J. Soc. Chem. Ind. 1908, 1112; Fr. Pat. 390673, 1908). Carbon monoxide passed over heated sodium or potassium hydroxide, soda lime, or calcium hydroxide, yields a formate and hydrogen, together with methane and ethylene. Carbon monoxide may be converted into hydrogen and hydrocarbons to the extent of 99·5 p.c. by passage over hot lime several times, and it is suggested that in this way illuminating gas might be freed from this toxic constituent (Vignon, Bull. Soc. chim. 1911, [iv.] 9, 18).

Properties.—Colourless gas of metallic odour and taste, combustible, non-supporter of combustion. Absorbed by carbon, by several metals, and by a solution of cuprous chloride in hydrochloric acid or ammonia. It acts as an energetic reducer. It is a highly poisonous gas, producing giddiness, and ultimately asphyxia when inhaled. 0·43 p.c. in air is fatal to man (Mosso, J. Gas Lighting, 1902, 80, 1334); 0·2 p.c. is also poisonous if breathed for any time.

When carbon monoxide is passed over dry silver oxide, the latter is reduced thus: $CO + Ag_2O = Ag_2 + CO_2$. Ammoniacal silver oxide is also reduced, and the reaction may be employed for the detection of small quantities of carbon monoxide in air (Dejust, Compt. rend. 1905, 140, 1250; Berthelot, *ibid.* 1891, 112, 597; Habermann, Zeitsch. angew. Chem. 1892, 324). It reduces Barreswil's (Fehling's) solution, and in contact with metallic copper moistened with aqueous potassium hydroxide is rapidly oxidised when mixed with air. The copper is converted into a peroxide, Cu_2O_3 or CuO_2, which is the active oxidising agent. The rate of oxidation is increased when the copper surface is coated with iridium.

0·02 p.c. carbon monoxide may be detected by the decolouration of a mixture of silver nitrate, and weak permanganate solution acidified with nitric acid (Merwet, Compt. rend. 1897, 124, 621).

According to Gréhant (*ibid.* 1891, 113, 289; 114, 309), 1 part of carbon monoxide may be detected in 10,000 parts of air, by aspirating the air through dog's blood, and testing the respiratory capacity of the blood before and after the experiment. When the air is passed under a pressure of 5 atmospheres, the test becomes still more delicate. It can also be detected by passing the gas through palladium chloride, when a metallic precipitate is formed and the colour indicates the quantity present. $\frac{1}{20000}$ to $\frac{1}{50000}$ carbon monoxide can be detected in the atmosphere by passing several litres of the suspected air through iodic acid, when the following reaction occurs :—

$$5CO + 2HIO_3 = 5CO_2 + H_2O + I_2$$
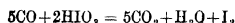
The iodine is absorbed in chloroform or carbon disulphide, when the relative tint indicates the quantity of carbon monoxide, or else the carbon dioxide is absorbed by standard potash solution and the carbon monoxide calculated (Gautier, Compt. rend. 1898, 126, 793, 871, 931, 1299; St. Martin, Compt. rend. 14, 1036; Kinnicutt and Sandford, J. Amer. Chem. Soc. 1900, 22, 14; Fillanger, Chem. Zeit. 1903, 27, Rep. 126; Levy and Pécoul, Compt. rend. 1905, 140, 98; Fr. Pat. 349714, 1904; 142162, 1906; • Morgan

and McWhorter, J. Amer. Chem. Soc. 1906, 29, 1589; Goutal, Ann. Chim. anal. 1910, 15; Graham and Winmill, Chem. Soc. Trans. 1914, 105, 1996; Sinnatt and Cramer, Analyst, 1914, 163; Froboese, Zeitsch. anal. Chem. 1915, 54, 1; Graham. J. Soc. Chem. Ind. 1919, 10 T.).

Carbon monoxide is oxidised quantitatively to carbon dioxide by passing it over yellow mercuric oxide heated to 100° (Moser and Schmid, Zeitsch. anal. Chem. 1914, 53, 217); Clowes recommends the flame cap test as an accurate and rapid method for detecting carbon monoxide (Brit. Assoc. Report, Chem. Zeit. 1896); whilst to detect the presence of carbon monoxide in mines, Haldane and also Herman (J. Soc. Chem Ind. 1896, 854) recommend the use of mice, which are very rapidly affected by small quantities of carbon monoxide. For a method of determining small quantities of carbon monoxide in hydrogen as used for ammonia synthesis, *see* E. K. Rideal and Taylor, Analyst, 1919, 89.

According to Leblanc (Ann. Chim. Phys. [3] 5, 223), it is chiefly the presence of this gas that causes the poisonous action of air in which charcoal has been burnt. The gases from a charcoal fire may contain up to 1·8 p.c. of carbon monoxide, those from a petrol engine 7·32 p.c. (in these gases the quantity of carbon monoxide exceeds that of the carbon dioxide), whilst the combustion products from gas-heaters contain from 1 part in 15,000 to 0 3 p c., according to the supply of air to the burner. A small proportion of carbon monoxide in a dusty atmosphere constitutes a dangerously explosive mixture. It combines with the red colouring matter of the blood-forming carboxyhæmoglobin, and may be recognised by its absorption spectrum, which is almost identical with that of oxygenated blood, and is characterised by two bands between D and E. On the addition of ammonium sulphide, these disappear in the case of oxygenated blood, and the spectrum shows one band midway between D and **E**, but remains unchanged if carbon monoxide is present (Vogel, Ber. 11, 235; Hoppe-Seyler, Zeitsch. anal. Chem. 3, 439; also Preyer, J. 1867, 802; Nawrocki, J. 16, 640; Gréhant, Compt. rend. 87, 193; St. Martin, *ibid.* 1892, 1 4, 1006). According to Nicloux (*ibid.* 1898, 126, 1526, 1595), carbon monoxide is a normal constituent of dog's blood, but this has been denied by Buckmaster and Gardner (Proc. Roy. Soc. B, 1909, 81, 515). Carbon monoxide burns ordinarily with a blue flame, which, by previous heating, becomes red, generating carbon dioxide. The temperature of its flame in air is about 1400° (Valerius, J. 1874, 58). According to Wieland (Ber. 1912, 45, 679), formic acid is an intermediate product in the combustion of carbon monoxide, and can be detected by allowing the flame to play upon ice. When dry it is not changed by the electric current nor by ignited platinum wire, but when standing over water it is decomposed by a glowing platinum spiral (Buff and Hofmann, Chem. Soc. Trans. 1860, 12, 273). When not absolutely dry, it may be exploded with oxygen by the electric spark or by platinum wire heated to 300° or by spongy platinum at ordinary temperatures. 2 vols. CO unite with 1 vol. O, forming 2 vols. CO_2.

• Dixon (Phil. Trans. 1884, 617) has shown that no action takes place when a spark is passed into a mixture of perfectly dry carbon monoxide and oxygen, but that a mere trace of moisture renders the mixture explosive. The combination takes place very slowly in presence of small quantities of steam, and increases in rapidity with the quantity of steam present. Probable reactions :

$$2CO + 2H_2O = 2CO_2 + 2H_2$$
$$2H_2 + O_2 = 2H_2O$$
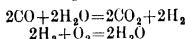
Hence the steam acts as a carrier of oxygen to carbon monoxide (v. Dixon, Chem. Soc. Trans. 49, 94).

Small quantities of other, gases than steam were tried : if the gas contained hydrogen, explosion occurred, if the gas contained no hydrogen, no explosion occurred. When a mixture of carbon monoxide and steam is heated to about 600°, a portion of the carbon monoxide is oxidised. If the carbon dioxide is removed as it is formed, the whole may be oxidised L. Meyer's experiments (Ber. 19, 1099) seem to prove that a dry mixture of carbon monoxide and oxygen can be exploded if a very strong spark is used, and a sufficiently high temperature then obtained, and if the gases are under considerable pressure. When sparks from an induction coil are passed through a mixture of carbon monoxide and steam, carbon dioxide, a little formic acid, and sometimes carbon, are formed (Dixon, Chem. Soc. Trans. 49, 94). When to a mixture of dry carbon monoxide and hydrogen, oxygen insufficient for complete combustion is added, and the mixture exploded by the spark, carbon dioxide and steam are formed in a ratio dependent upon the shape of the vessel and the pressure up to a certain limit, called the 'critical pressure.' Above this pressure the ratio of the formation of carbon dioxide and water is independent of the shape of the vessel. The critical pressure becomes lower the larger the quantity of oxygen used. The ratio $CO + H_2O : CO_2 + H_2$ remains constant so long as the vol. of the hydrogen is more than twice that of the oxygen, provided no steam condenses, and the pressure is above the critical pressure. When the vol. of hydrogen is less than twice the vol. of oxygen, the above ratio diminishes. The presence of an inert gas increases the formation of carbon dioxide and diminishes that of water, hence it lowers the value of the ratio $CO + H_2O : CO_2 + H_2$. This ratio is called the ' coefficient of affinity ' of the reaction (Dixon, Phil. Trans. 1884, 617 ; Chem. Soc. Trans. 49, 94). According to Brodie, when carbon monoxide and hydrogen are submitted to the action of the silent discharge, marsh gas is formed by synthesis ; when pure and dry carbon monoxide is circulated through the induction tube, it is decomposed, carbon dioxide being formed together with other ' oxy-carbons ' of the formulæ C_4O_3 and C_5O_4 (Brodie, Proc. Roy. Soc. 21, 245).

Carbon monoxide is converted into carbon dioxide under the influence of nascent oxygen from chromic acid (Ludwig, Annalen, 142, 47), but not by ozone, either in diffused daylight or in direct sunshine (Remsen and Southwark, Amer. J. Sci. [3] 11, 136). It is likewise oxidised by palladium charged with hydrogen in presence of oxygen and water (Traube, Ber. 15, 2325, 2854 ; 16, 123 ; Remsen and Kejser, ibid. 17,

83 ; Wieland, Ber. 1912, 45, 679) ; by mixing with oxygen and passing over platinum black ; by nitric oxide (Hasenbach, J, pr. Chem. [2] 4, 1) ; by heating with metallic oxides and with many oxysalts. Adsorbed on ' activated' platinum it is rapidly converted into carbon dioxide in contact with oxygen.

When passed over finely divided metals, such as nickel, cobalt, or iron, the quantity of carbon dioxide formed depends on the temperature and the metal (Zimmermann, Ber. 1903, 36, 1231 ; Sabatier and Senderens, Bull. Soc. chim. 1903, 29, 294 ; Berthelot, Compt. rend. 1891, 112, 594 ; Van Breakedensen and Horst, Rec. trav. chim. 19, 27 ; Smits and Wolff, Zeitsch. physikal. Chem. 1903, 45, 199 ; Charpy, Compt. rend. 1903, 137, 120 ; Boudouard, ibid. 1899, 128, 1522). In some cases a volatile carbonyl compound is formed of the type $M(CO)_4$ (Lange and Quincke, Chem. Soc. Proc. 1890, 112 ; 1891, 117 ; Wartha, Chem. Zeit. 1891, 15, 915 ; Garnier, Compt. rend. 1891, 113, 189 ; Gautz, Bull. Soc. chim. 1892, 13, 278 ; Bertholet, 1892, 431, 134 ; Sabatier and Senderens, l.c.). According to Gautz (Compt. rend. 1892, 114, 115), at 400° carbon monoxide reacts with manganese and iron, thus : $CO + Mn = MnO + C$. Carbon monoxide passes through cast and wrought iron when heated to redness, and, according to Sieverts and Krumbhaar (Ber. 1910, 43, 893), it dissolves in nickel and cobalt, but not in copper.

Minute quantities of carbon monoxide reduce gold chloride, and also gold, silver, and mercury oxides (Fay and Seeker, J. Amer. Chem. Soc. 1903, 25, 641). Brunck (Zeitsch. angew. Chem. 1912, 25, 2479) has proposed to employ its reducing action on palladium chloride (sodium-palladous chloride) as a method of estimating small quantities of carbon monoxide.

When an electric spark is sent through a mixture of ammonia and carbon monoxide, ammonium cyanate is chiefly formed (Northall Laurie, Chem. Soc. Trans 1905, 433).

Pure carbon monoxide forms a colourless transparent liquid under 200–300 atmospheres at –139°, and solidifies to a snowy mass in vacuó at –211° (Olszewski, Compt. rend. 99, 706 ; 100, 350 ; Wroblewski and Olszewski, Ann. Chim. Phys. [6] 1, 112).

Carbon monoxide combines with potassium at about 80° to form an explosive compound, KCO (Brodie, Chem. Soc. Trans. 1860, 12, 269). It is rapidly absorbed by a solution of cuprous chloride in ammonia or hydrochloric acid, by which means it may be directly estimated in a gaseous mixture (cf. Thomas, Chem. News, 37, 6). According to Manchot and Brandt (Annalen, 1909, 370, 286), it forms the compound $CuCl \cdot CO, 2H_2O$, with copper chloride, and the $2H_2O$ can be replaced by $2NH_3$. It is also absorbed by moist silver oxide. It unites directly with chlorine, forming phosgene gas (Schützen-berger, Zeitsch. f. Chem. [2] 4, 321). It is absorbed by heated potassium hydroxide at about 200°, forming potassium formate (Berthelot, Ann. Chim. Phys. [3] 61, 463). Fröhlich and Geuther (Annalen, 202, 317) recommend passing carbon monoxide over soda-lime for this purpose. It combines with sulphur to form carbon oxysulphide ; with platinum tetrachloride to form $C_2O_3PtCl_4$ and $C_2O_2PtCl_4$ (Schützenberger, Ann. Chim. Phys. [4] 21, 430). It is rapidly absorbed

F

by anhydrous hydrocyanic acid cooled by a freezing mixture, two layers being formed, but the gas is evolved on removing the tube from the mixture (Böttinger, Ber. 10, 1122). It acts on metallic alcoholates with formation of acids by synthesis (Geuther, Annalen, 202, 288; Schroeder, *ibid.* 221, 34).

Carbon monoxide has been used in electrolytic cells by Haber and Moser (Zeitsch. Elektrochem. 1905, n. 593).

Carbon dioxide, *Carbonic anhydride, Carbonic acid, Gaseous.*—Sp.gr. 1·52909 (Rayleigh); 1·52894 (Leduc). V.D. 22·42 at 800°; 21·2 at 1180° (Meyer and Goldschmidt, Ber. 1882, 15, 1165).

Specific heat (const. vol.), 0·33 (equal vol. air=1); 0·2169 (equal wt. air =1) (Regnault, Compt. rend. 36, 676, etc. ; Wiedemann, Pogg. Ann. 157, 24). Ratio of specific heat at const. press. to specific heat at constant volume =1·29—1·305 (Amagat and Röntgen, Compt. rend. 71, 336; 77, 1325). Coefficient of expansion=0·0037 (Regnault, Magnus, and Joly) PV/P_1V_1 = 1·00722 (Regnault, *ibid.* 29, 975); at 200° carbon dioxide obeys Boyle's Law (Amagat, *ibid.* 68, 1170; 73, 183)

u_C =1·000395; u_E =1·000356; u_O =1·000496 (Croullebois, Ann. Chim. Phys. [4] 20, 136; Chapman and Rivière, Compt. rend. 103, 37). Heat of formation (const. press.) (C+O_2) =96·96; (CO+O)=67·96: heat of formation (const. vol.) (C+O_2)=96·96; (CO+O)=67·67; (C+O_2+Aq)=102·84; (CO+O+Aq)=73·84; (CO$_2$ + Aq) = 5·88; (CO$_2$Aq + nNaOHAq) =11·016 (n=1); 20·184 (n=2); 20·592 (n=4) (Thomsen).

Solubility of CO_2 in water (Bunsen, Annalen, 93, 1):—

at 0°=1·7967	at 7°=1·3339	at 14°=1·0321
1°=1 7207	8°=1·2809	15° =1·0020
2°=1·6481	9° =1·2311	16°=0 9753
3°=1·5787	10° =1·1847	17°= 0·9519
4°=1·5126	11°=1·1416	18° 0·9318
5°=1·4497	12°=1·1018	19° =0·9150
6°=1·3901	13°=1·0653	20° =0·9014

whence absorption coefficient

$$=1·7967-0·077611+0·0016124t^2$$

For influence of non-electrolytes on the solubility of carbon dioxide in water, *see* Usher (Chem. Soc. Trans. 1910, 97, 66).

Solubility of CO_2 in alcohol :—

at 3·2°=4·0442	at 14·3°=3·3257
6·8°=3·7374	18° =3·0391
10·4°=3·4875	22·6°=2·8277

whence absorption coefficient

$$=4·32955-0·09395t+0·00124t^2$$

For the solubility of carbon dioxide in beer, *see* Langer and Schultze (Zeitsch. fur des ges. Brauwesen, 1879, 2, 369); Emslander and Freundlich (Zeitsch. physikal. Chem. 1904, 49, 317); Findlay and Spen (Chem. Soc. Trans. 1911, 1313).

Liquid.—Sp.gr. 1·057 at -34°; 0·966 at -11°; 0·84 at+11°; 0·726 at +22·2° (Cailletet and Mathias, Compt. rend. 102, 1202). Coefficient of expansion very large, 120 vols. at -20° become 150 vols. at +30° (Thilorier, Ann. Chim. Phys. 60, ii. 427).

Critical temperature 30·9° (Andrews, Phil.

Trans. 1869, 575), 31·35° with a corresponding pressure of 72·0 atmos. (Amagat). 31·9° and a pressure of 77 atmos. (Dewar). Vap. press. in atmos. (Regnault) 17·1 at −25°; 30·9 at −5°; 35·4 at 0°; 40·5 at +5°; 52·2 at 15°; 66 at 25. B.p. −78·2° at atmos. press. (Regnault).

Solid.—Sp. gr. slightly under 1·2 (Landolt, Ber. 1884, 17, 309). Vap. press. in atmos. (Faraday) 5·33 at −57°; 2·2 at −70·5°; 1·14 at −99·4°. When solid CO_2 is exposed to the air, the temperature remains constant at −78° to −79° (Villard and Jarry; Pouillet; Regnault).

Carbon dioxide was known to Paracelsus and Van Helmont, and was carefully studied by Cavendish. Its true composition was first demonstrated by Lavoisier in 1775. It was liquefied by Davy and solidified by Thilorier. It is formed by the combustion of carbon in oxygen or air (Dixon, Chem. Soc. Proc. 1899, 118; Nauwaan, Zeitsch. angew. Chem. 1896, 200). According to Potter (Proc. Roy. Soc. 1908, 80, B, 239), amorphous carbon, such as charcoal, lampblack, coal, &c., when exposed to air, is slowly oxidised by the agency of bacteria, to carbon dioxide, the amount of which increases with rise in temperature. The temperature at which carbon will form carbon dioxide and monoxide, when heated in oxygen, depends largely on whether the temperature has been reached by heating or cooling (Manville, Compt. rend. 1906, 142, 1190). The presence of moisture is necessary for the combustion of carbon in oxygen (Brereton Baker, Chem. Soc. Trans. 1885, 349; Rhead and Wheeler, Chem. Soc. Trans. 1912, 101, 846; *ibid.* 1913, 103, 1210). It is a constant product of ordinary processes of combustion. It is also formed by the respiration of animals, in various processes of fermentation, and by the decay of animal and vegetable substances. It is evolved from fissures in the ground in volcanic districts, and from the craters of active volcanoes, and exists in solution in natural waters, some of which contain it in such quantities as to effervesce. It is found also in mines, quarries, wells, and caverns, particularly in limestone districts. It is a constant constituent of the atmosphere, which contains on the average about 0·034 p.c. The air in streets often contains as much as 0·05 to 0·09 p.c. In crowded rooms it may reach 0·3 p.c. It is further produced by the decomposition of carbonates either by the action of heat or of stronger acids, and is frequently formed when organic bodies are subjected to high temperatures. In the reduction of many metallic oxides by carbon: by burning carbon monoxide; by heating together carbon monoxide and steam; and by the action of steam on calcium carbonate at red heat ; by heating a mixture of potassium dichromate and sodium carbonate.

Best prepared by acting on chalk, marble, or magnesite with dilute hydrochloric acid solution. The gas may be collected over water or by displacement of air. On the large scale it is obtained by heating chalk or limestone to redness in iron or earthen vessels (in lime burning) or by burning charcoal. It is manufactured also as a by-product in the combustion of fuel. Also pure on large scale by heating carbonates with steam (J. Soc. Chem. Ind. 3, 568).

According to Thom and Pryor (*ibid.* 1909,

1087), pure carbon dioxide can be manufactured from limestone by the following process: The limestone is heated in closed retorts around a central combustion chamber, beneath which is a furnace, the whole apparatus being enclosed in a casting which excludes air from the retorts. Superheated steam is admitted to the retorts at their lower ends, and this decomposes the limestone and carries the carbon dioxide through outlets at the top of each retort, leading to a collecting gas main running round the top of the casting. The retorts have closely fitting mouth-pieces, at which they are charged and discharged respectively. By a system of air and waste-gas flues, perfect combustion and the fullest use of heat from the waste gases is ensured (Eng. Pats. 20102, 24632, 1908).

Carbon dioxide is obtained commercially from natural waters from the Saratoga springs in New York, and also in South Germany. In North Germany the gas is obtained by the combustion of coke, which is generally considered to be the cheapest and best commercial method of producing carbon dioxide. Coke is burnt in a generator, A (Fig. 14); the products pass into a combustion chamber, B, into which hot air is

it leaves, almost saturated, by the overflow siphon and accumulates in the tank L. The pump J then drives it through the tubular vessels M and O (where it is heated to 60° and 90° respectively) into the heater C, where its temperature is raised to 100°. The 'poor ley' circulates in the opposite direction back to the tank K. The carbon dioxide evolved from C passes into a cooler, then to a gasholder (Schwatolla, Zeitsch. angew. Chem. 1900, 1284).

Other methods of obtaining carbon dioxide from coke are described by Candia and Merlini (J. Soc. Chem. Ind. 1908, 847), Leslie (*ibid.* 1905, 240), Gravillon (*ibid.* 1900, 164; Eng. Pat. 8377, 1904), and many others.

Numerous patents also exist for obtaining carbon dioxide from furnace gases and from lime kilns, most of which depend upon its absorption by potassium or sodium carbonate solution, from which it is then boiled off (Rylands, J. Soc. Chem. Ind 1892, 1005).

Leslie (*ibid.* 1907, 688) describes a somewhat different method. The furnace gases pass from a purifier to a pump, where they are
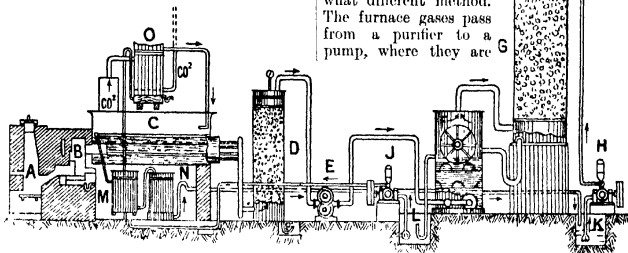
FIG. 14.

admitted to complete the combustion, thus oxidising all the carbon monoxide and hydrogen sulphide. The hot gases now pass through tubes contained in the vessel C, thus heating and decomposing the bicarbonate solution contained in this vessel. The gas now passes through one or more wash towers, D, containing limestone over which water trickles, and is freed here from dust and sulphur dioxide. E is a blower or fan, which sucks the gas through the furnace and drives it through the absorbing apparatus. F is a rectangular vessel filled with potash ley, and provided with a number of semi-circular baffle plates, so arranged that the gas accumulates under each successively, thus remaining exposed for a considerable time under the pressure of the column of fluid to a large surface of liquid. The absorption is further helped by an agitator, which throws the liquid into the upper portion of the vessel. From F the gas passes into the tower G, where the absorption is practically completed, and then leaves the apparatus. The circulation of the potash ley starts from the tank K, whence it is pumped by H through the Körting's jets into the upper part of G, which is thus filled with fine spray. The siphon at the bottom of the tower delivers the partially saturated ley into F, which

compressed, after which they are cooled in a heat interchanger, from which they are led to a drying vessel, containing calcium chloride, into a refrigerator, in which the carbon dioxide is condensed to snow; the other gases, still above their critical temperature, are passed back through the interchanger, whilst the carbon dioxide is liquefied and drawn off into tubes and cylinders (Eng. Pat. 11902, 1906).

A method of obtaining sterilised carbon dioxide, with disinfecting properties, is described by Bouchaud-Praceiq (J. Soc. Chem. Ind. 1908, 994).

Many attempts have been made to collect the carbon dioxide given off during fermentation processes, and some of these have been successful from a commercial and industrial point of view.

Mixtures of a carbonate or bicarbonate with a salt or double salt, which is readily hydrolysed in aqueous solutions, have been prepared for the generation of carbon dioxide (Menter and Sedlitzky, J. Soc. Chem. Ind. 1908, 1151; Eng. Pat. 14863, 1908).

Ageron and Remy (J. Soc. Chem. Ind. 1906, 847) have prepared a compound by heating a mixture of magnesium sulphate and sodium sulphate or bisulphate with sulphuric acid,

which they use as a substitute for acids in liberating carbon dioxide from carbonates.

Carbon dioxide is a colourless, inodorous gas, neither combustible nor a supporter of combustion. Strongly heated potassium or sodium and brightly burning magnesium burn in carbon dioxide.

When quite dry it has no action upon litmus, but if moisture be present the litmus is coloured wine-red. The colour disappears on exposure to air, owing to escape of the gas. Passed into lime-water, carbon dioxide renders it turbid, owing to the formation of calcium carbonate, but if the gas be in excess, the neutral carbonate is converted into an acid carbonate, and the liquid becomes clear.

Carbon dioxide is rapidly absorbed by a solution of caustic potash.

Between $-85°$ and $+54°$ absolutely dry carbon dioxide does not react with absolutely dry alkali hydroxides. At or above $54°$, the dry substances do react, and at $85°$ a trace of moisture at once starts the reaction, which is completed very rapidly (Moissan, Compt. rend. 1903, 136, 723). It is also absorbed by sulphuric acid [$100a=926$], where $a=$ Bunsen's absorption coefficient (Bohr, Chem. Zentr. 1910, ii. 1414).

Its solution in water has a sp.gr. 1·0018. It has a slightly acid taste, colours litmus wine-red, and partially neutralises alkalis and dissolves carbonates of barium, strontium, calcium, and magnesium, &c.

The solution corrodes iron. Kröhnke (J Soc. Chem. Ind. 1900, 520) found that water containing about 40 mgrms. of CO_2 per litre reduced iron pipes in a short time from 26 mm. to 7 mm. diameter, owing to the formation of a brown crust, the pipe itself being corroded to a depth of 1–3·5 mm.

Its solution in water probably contains carbonic acid H_2CO_3. At ordinary temperatures, and under 1 atmosphere, the mass of carbon dioxide dissolved increases as the pressure. But at pressures of 2, 3, or more atmospheres, the mass of carbon dioxide dissolved is less than that calculated by Dalton and Henry's law (v. Khanikoff and Louguinine, Ann. Chim. Phys. [4] 11, 412). By the action of carbon dioxide under pressure on water at low temperatures, the crystalline hydrates $CO_2,6H_2O$ (Villard, Compt. rend. 1894, 119, 368), $CO_2,8H_2O$, and $CO_2,9H_2O$ (Hempel and Seidel, Ber. 1898, 31, 2997) have been obtained.

Water which has been saturated with carbon dioxide under pressure gives it up as soon as the pressure is removed. This property is made use of in the manufacture of effervescing drinks and aërated waters (v. AËRATED WATERS).

Under the same pressure the volume of gas absorbed by water diminishes as the temperature rises, the whole of the gas being expelled at boiling heat. Hence carbonic acid water, holding an earthy carbonate in solution, deposits it when the water is boiled. This is the cause of the furring of kettles, boilers, &c., in which spring or river waters have been boiled.

Potassium burns in carbon dioxide at a red heat with a red incandescence, depositing charcoal mixed with potassium carbonate. Sodium decomposes it in a similar manner, as do phosphorus and boron in presence of an alkali.

It is decomposed by the electric spark into carbon monoxide and oxygen, if hydrogen, or mercury, or some other metal is present to combine with the oxygen, otherwise the carbon monoxide and oxygen recombine to form carbon dioxide (Collie, Chem. Soc. Trans. 1901, 1063).

Partly decomposed by electric sparks, a condition of equilibrium is attained when change of CO_2 into $CO + O$ equals that of $CO + O$ into CO_2 (Dixon and Lowe, Chem. Soc. Trans. 47, 571).

Carbon dioxide is decomposed by the silent electric discharge, the amount of decomposition varying with the degree of dryness of the gas, the intensity of the discharge, and the form of ozoniser employed, but in all cases a diminished pressure of the gas results in a greater decomposition (Holt, Chem. Soc. Proc. 1908, 24, 271).

Ultra-violet light decomposes dry carbon dioxide at the ordinary temperature into carbon monoxide and oxygen; similar results are obtained by the action of radium emanations (Herschfinkel, Compt. rend. 1909, 149, 395; Ramsbottom, Chadwick, and Chapman, Chem. Soc. Proc. 1906, 23).

It is partly changed to carbon monoxide and oxygen by heating to 1300° in a porcelain tube (Deville, Compt. rend. 56, 729; also Berthelot, ibid. 68, 1035).

When heated at 350° with hydrogen over reduced nickel or cobalt, it is completely reduced to methane (Sabatier and Senderens, ibid. 1902, 134 689).

With carbon at 500°–650°, it forms carbon monoxide, equilibrium being reached when the mixture of gases contains 61 p.c. unreduced CO_2 (Boudouard, ibid. 1899, 128, 824, 1524; 1905, 141, 252).

Mixed with hydrogen and heated to bright redness, or submitted to induction sparks, carbon monoxide and water are formed; if the water is removed, the whole is converted to carbon monoxide (Dixon, Chem. Soc. Trans. 49, 94; Gautier, Bull. Soc. chim. 1906, 35, 929). A mixture of carbon dioxide and hydrogen passed over red-hot pumice yields carbon and water (Dubrunfaut, Compt. rend. 74, 125).

Mixed with sulphur-vapour and passed through a red-hot tube it gives carbon monoxide, sulphur dioxide, and a little carbon oxysulphide (Berthelot, Bull. Soc. chim. [2] 40, 362). Passed through a red-hot tube with sulphuretted hydrogen, it forms carbon monoxide, water, and sulphur (Köhler, ibid. 11, 205). Reduced to carbon monoxide by hydrogen, iron, and zinc or copper which has occluded hydrogen (Tissandier, Compt. rend. 74, 531; Schrötter, Wied. Ann. 34, 27); by potassium cyanide (Filoart, Chem. News, 54, 88); by protoxides of iron and tin (Wagner, Zeitsch. anal. Chem. 1879, 559); and partially by ferrous sulphate, and a little water in a closed tube (Horsford, Ber. 6, 1390).

Carbon dioxide is reduced to carbon by heating with potassium, sodium, magnesium, or silicon (Schmöle, J. Soc. Chem. Ind. 1895, 1060). Alkaline carbonates heated strongly with phosphorus or boron give carbon dioxide, which is reduced to carbon (Tennant, Crelles Annalen, [1793] 1, 158; Dragendorff, J. 1861, 111; Leeds, Bull. Soc. Chim. 12, 1834 and 2131); decomposes moist potassium iodide at high temperatures, yielding hydriodic acid (Papasogli, Gazz. chim. ital. 1881, 227); it also decomposes alkaline aluminates (Ditte, Compt.

rend. 1893, 116, 386) ; and, according to Moore, liberates nitrous acid from nitrites (J. Amer. Chem. Soc. 1904, 26, 959). Solution of carbon dioxide in water yields sodium formate with metallic sodium (Kolbe and Schmidt, Annalen, 119, 251). Carbon dioxide is assimilated by the chlorophyll of plants under the influence of sunlight, carbon being abstracted and oxygen set free. Carbon dioxide diffuses through caoutchouc (Kobbe, Chem. Zeit. 1890, 14. 1142).

The specific heat of carbon dioxide is greater at high than at ordinary temperatures (Berthelot and Vieille, Compt. rend. 98, 770 and 852). According to Hoppe-Seyler (Zeitsch, physikal. Chem. 10, 201, and 10, 401), the carbonic acid and marsh gas found in water-logged soils is due to a widespread process of fermentation of cellulose.

In any working- or living-room the carbon dioxide should not be more than 10 volumes per 10,000 of air.

To estimate the carbon dioxide in air, a measured sample of the air is passed through a known quantity of barium hydroxide, coloured with phenolphthalein, and by noting the quantity of air needed to decolourise the hydroxide the carbon dioxide can be calculated. The method is sometimes modified by using a limited volume of air, and titrating the hydroxide remaining unneutralised (Ballo, Ber. 1884, 1097 , Wiener, Monatsh. 1894, 15, 429 ; Henriet, Compt. rend. 1896, 123, 125 ; Woodman, J. Amer. Chem. Soc. 1903, 25, 150 ; Jean, Compt. rend 1902, 135, 746 ; J. Pharm. Chim. 1903, 27, 418 ; Pécoul and Levy, J. Soc. Chem. Ind 1906, 655 ; Davies and McLellan, ibid. 1909, 232).

Carbon dioxide is used extensively in the arts for the manufacture of aerated waters, in sugar manufacture for separating lime from the juice of the sugar-cane, in bread making, and for raising and clarifying beer.

It is also employed for protecting wines from moulds and acetifying organisms. It preserves their aroma and bouquet, and makes the wine fresher, sweeter, and stronger. Wines can also be revivified by the gas (Piaz, J. Soc Chem. Ind. 1894, 266 ; 1903, 644 ; Pini, Bull. de l'Assoc. des Chim. 1898, 15, 741). It also possesses antiseptic properties and retards the putrefaction of meat (Kolbe, J. pr. Chem. [2] 28, 61). It has also been proposed to use it as a motive power where fuel is expensive (Herbert, Chem. Zentr. 1885, 543, 558, 572).

Mixed with acetylene (about 5-8 p.c.), it decreases the smokiness of the flame and prevents the clogging of the burners (J. Gas Lighting, 1898, 72, 916).

Liquid carbon dioxide (Baichner, Zeitsch. physikal Chem. 1906, 54, 665) can be obtained in large quantities by an apparatus described by Thilorier (Annalen, 30, 122). Natterer compressed carbon dioxide by a specially constructed air-pump (J. pr. Chem. 35, 169) ; *v.* also Gore, Phil. Trans. 1861, 63). It is prepared from bisulphates by the action of carbonates, the apparatus consisting essentially of a leaden vessel containing a solution of the bisulphate and having a stirring apparatus and gear fixed air-tight to it. By means of a tube and pump an equivalent quantity of calcium carbonate (obtained as a waste product in the manufacture of caustic soda) suspended in water in a second vessel is forced

in and the stirrer set in motion. The liberated carbon dioxide is dried and passed into a gasometer from which it is afterwards condensed. An apparatus is also described which allows the evaporation and expansion of liquid carbon dioxide to take place round a tube containing a solution of calcium chloride. The latter is so cooled that it may be used for the manufacture of ice. The carbon dioxide thus used is passed over moist sodium carbonate, converting it into bicarbonate, which may be again used in the carbonic acid manufactory (Thomas, Zeitsch. angew. Chem. 1900, 386). (For description and figure of apparatus for liquifying CO_2 and for bottles in which it is stored and sold, *see* Sisson, J. Soc. Chem. Ind. 1904, 242.)

Liquid carbon dioxide may be bought in iron or steel bottles containing 8 kilos. (about 4000 litres of the gas at ordinary temperature and pressure), costing about 1 sh. per kilo. It furnishes the cheapest means for aerating waters, and is used for raising sunken ships, for driving torpedoes, for extinguishing fires, for cooling purposes, and, as ' Pictet's fluid,' for freezing machines, and by the firm of Krupp, in Essen, for the condensation of steel and other metals, and is further suggested as a motive power for tramcars and balloons (J. Soc. Chem. Ind. 4, 610).

It is also used for making carbonates and other chemical products, for filtering and sterilising organic liquids (d'Arsonval, Compt. rend. 1891, 112, 667), and in Germany for the generation of pressure on storage casks of beer to the faucets above where the beer is drawn for consumption. In Engineering, Dec. 3, 1903, a description is given of its use in railway signalling in outlying stations, to supply the motive power for working the signals, so as to avoid the expense of compression machinery or of long lengths of connecting pipes.

Liquid carbon dioxide is colourless, very soluble in alcohol, ether, and volatile oils, but does not mix with water. When the pressure is suddenly relieved, part of the carbon dioxide immediately vaporises, producing sufficient cold to solidify the remainder. Landolt allows the liquid to evaporate freely into woollen bags, and compresses the solid carbon dioxide in conical wooden moulds by wooden pistons (Ber. 17, 309) ; *cf.* Purcell (J. Soc. Chem. Ind. 1892, 936 ; Eng. Pat. 13684, 1891). A vessel for storing solid carbon dioxide is described by Heyl and Wultze (J. Soc. Chem. Ind. 1904, 1215 ; Eng. Pat. 344957, 1904).

An apparatus for obtaining small and large quantities of solid carbon dioxide is described by Fechlu (J. pr. Chem. 1903, 67, 423 ; J. Soc. Chem. Ind. 1903, 626) ; also by Elsworthy (J. Soc. Chem. Ind. 1905, 1231). (For an apparatus for collecting solid carbon dioxide, *v.* Ducretet, Compt. rend. 99, 235.)

Solid carbon dioxide is a white, flocculent, snow-like mass, melting at −56·7° at 5 atmospheres pressure, and may be left exposed to the air for some time without sensible evaporation. An air or spirit thermometer immersed in it sinks to −79° ; it can, however, be placed on the hand without any acute sensation of cold. By mixing with ether its refrigerating power is greatly increased. This is denied by Villard and Jarry (l.c.) but the temperature sinks to

—85° when it is mixed with chloroform. The temperature can readily be reduced to —90° by passing a current of air through the mixture. At 5 mm. pressure the temperature of solid carbon dioxide soon falls to —125°.

Magnesium powder burnt in a dish of solid CO_2 deposits carbon (Brünner, Ber. 1905, 38, 1432).

COMPOUNDS OF CARBON.

Carbon tetrabromide or **Tetrabrommethane** CBr_4. White lustrous crystals of a character-istic pungent smell; m.p. 91°; b p. 189·5° with slight decomposition; b.p. 101° at 50 mm. without decomposition. Occurs in two enantio-tropic forms (Rothmund, Zeitsch. physikal. Chem. 1899, 664). Insoluble in water; soluble in alcohol, ether, and chloroform. Best ob-tained by action of bromine on carbon disulphide in presence of iodine (Bolas and Groves, Chem. Soc. Trans. 1870, 161 ; 1871, 773).

Carbon tribromide or **Hexabromide**, *Tetra-brommethylene dibromide* C_2Br_6. Small rect-angular prisms obtained by action of bromine on ethylene dibromide ; or by heating C_2HBr_5 with bromine and water at 170°. Soluble in carbon disulphide; insoluble in alcohol and ether. Decomposed at 200° into C_2Br_4 and Br_2 (Reboul, Annalen, 124, 271).

Carbon dibromide, *Tetrabrommethylene* C_2Br_4. White crystals ; m.p. 53° ; formed by action of nascent hydrogen on C_2Br_6 (Lowig, Annalen, 3, 292 ; Lennox, Chem. Soc. Trans. 1862, 14, 209).

Carbon bromide, *Dibromacetylidene* $C . CBr_2$, b.p. 76°. Prepared from tetrabromoethane by removal of two molecules of hydrobromic acid. Spontaneously inflammable in air and very explosive (Lemoult, Bull. Soc chim 1905, 43, 193). It contains a double bond (Lawrie, Amer. Chem. J. 1906, 36, 487).

Chlortribrommethane $CClBr_3$. Colourless plates ; m.p. 55° ; b.p. 160°. Prepared by heating chloroform with bromine at 250°, and retaining fraction distilling at 160° (Besson, Compt. rend. 1892, 114, 223).

Dichlordibrommethane CCl_2Br_2. Fine needles; m.p. 22° ; b.p. 135°. Obtained from chloroform by action of bromine as above, retaining the fraction of the product boiling at about 135° (Besson, l.c.).

Trichlorbrommethane CCl_3Br ; m p. —21° ; b.p. 104°. From chloroform and bromine (Besson, l.c.). From bromine and trichloracetic acid (J. H. van't Hoff, Ber. 1877, 678).

Chlorotribromethylene $CClBr : CBr_2$; m.p. 34° ; b.p. 203°–205° at 734 mm. (Denzel, ibid. 1879, 2208).

αα-**dichloro-***ββ*-**dibromoethylene** $CCl_2 : CBr_2$, b.p. 194° (Bourgoin, Bull. Soc chim. 1875, 116 ; and Denzel, Annalen, 1879, 208).

αβ-**dichloro-***αβ*-**dibromoethylene** $CClBr.CClBr$, b.p. 172° at 765 mm. (Swarts, Chem. Zentr. 1899, i. 588).

Trichlorobromoethylene $CCl_2 : CClBr$; m.p. —12° to —13° ; b.p. 145°–148° (Besson, Compt. rend. 1894, 119).

Chloropentabromoethane C_2ClBr_5 ; m.p. 170° Denzel, Ber. 1879. 2207).

αα-**dichloro-***αβββ*-**tetrabromoethane** $CCl_2Br.CBr_3$ '
Colourless crystals ; m.p. 180° (Denzel, Ber 1879, 2207).

αβ-**dichloro-***ααββ*-**tetrabromoethane** $CClBr_2.CClBr_2$
m.p. 191° (Swarts. Chem. Zentr. 1899, [1] 588).

αββ-**trichloro-***ααβ*-**tribromoethane** $CClBr_2.CCl_2Br$
m.p. 178°–180° (Besson, Compt. rend. 1894, 88).

αβββ-**tetrachloro-***αα*-**dibromoethane** $CClBr_2.CCl_3$
Prisms from alcohol ; smells like camphor. May be sublimed (Paternò, Gazz. chim. ital. 1, 593 ; Bourgoin, Bull. Soc. chim. [2] 23, 4 ; Gossner, Chem. Zentr. 1903, ii. 1053).

ααββ-**tetrachloro-***αβ*-**dibromoethane** · $CCl_2Br.CCl_2Br$
Tables from alcohol (Malaguti, Ann. Chim. Phys. 1846, 24 ; Gossner, Chem. Zentr. 1903, ii. 1053).

Fluorotribromomethane CBr_3F, a colourless, heavy, pleasant-smelling liquid, b.p. 107°/760 mm., obtained by heating carbon tetrabromide at 50°–60° with silver fluoride.

Difluorodibromomethane CBr_2F_2, a mobile liquid, b p. 24 5°/760 mm., m.p. below —80°, formed by the action of the preceding compound on silver fluoride (Rathsburg, Ber. 1918, 51, 669).

Carbon tetrachloride or **Tetrachlormethane** CCl_4 was first obtained by Regnault (Annalen, 1840, [33] 332), who obtained it by the action of chlorine on chlorform in sunshine :

$$CHCl_3 + Cl_2 = HCl + CCl_4$$

Dumas afterwards obtained it by the action of chlorine upon marsh gas (Annalen, 1840, [33] 187). It can also be prepared by passing carbon disulphide saturated with chlorine through a red-hot tube. The mixture of carbon tetra-chloride and sulphur chloride thus obtained is treated with potash or milk of lime and the tetrachloride distilled off (Kolbe, Annalen, 1843, 45, 41 ; 1845, 54, 146) The tetrachloride may contain carbon disulphide if that substance was in excess, or if the heat was insufficient. This may be removed by leaving the liquid for some time in contact with potash. Geuther removes the carbon disulphide by converting it into potassium xanthate by dissolving the mixture in alcohol, adding alcoholic potash so long as the liquid becomes darker in colour, and heating gently ; the unaltered tetrachloride is separated by water and purified by washing (Geuther, Annalen, 1858, 107, 212 ; and Selmitz-Dumont, Chem. Zentr. 1897, ii. 265).

The complete chlorination of carbon disul-phide and of many other carbon compounds can be more readily accomplished in the presence of a chlorine carrier. Thus, in the case of carbon disulphide, bromine has been used (Crump, Chem. News, 1886, 14, 154) and iodine, both alone (Morel, Compt. rend. 1877, 84, 1460) and in the presence of metallic iron (Serra, Chem. Xentr. 1899, ii. 1098) : antimony penta-chloride reacts with carbon disulphide alone, without the addition of chlorine. The mixture becomes hot, and on cooling deposits crystals of antimony trichloride mixed with sulphur, whilst carbon tetrachloride remains in solution (Hofmann, Annalen, 1860, 115, 264).

A large number of other substances can be used as catalytic agents, e.g. molybdenum pen-tachloride (Aronheim, Ber. 1876, 1788), the chlorides of phosphorus and arsenic, and also a

series of chlorides of metals, especially those of the iron group. In the presence of these substances, sulphur chloride reacts readily with carbon and excess of chlorine, giving carbon tetrachloride. A stream of chlorine is led over a red-hot mixture of charcoal and sulphur. Carbon disulphide is first formed, then carbon tetrachloride and sulphur monochloride; the latter then breaks up into chlorine and sulphur, and the process begins over again. The carbon tetrachloride prepared in this way is usually contaminated with sulphur chlorides and chlorethane compounds (Combes, Chem. Zentr. 1909, 1, 326 ; J. Soc. Chem. Ind. 1902, 272 and 1469). In the presence of manganese chloride the reaction can be carried out with precipitation of sulphur, which can be used to manufacture more carbon disulphide (Côte and Pierron, *ibid.* 1903, 962 : Febvre, *ibid.* 1905, 1189). Other carbon compounds beside carbon disulphide can be completely chlorinated. Thus chloroform heated with iodine chloride at 165° gives carbon tetrachloride (Friedel and Silva, Bull. Soc. chim. 1872, 537), the same reaction taking place, to a slight extent, in the presence of aluminium trichloride instead of iodine chloride (Monneyrat, *ibid.* 1898, 262).

Perchlormethyl formate, when treated with aluminium chloride in the proportion of 50 parts to 1 of chloride, also yields carbon tetrachloride $CClO_2 \cdot CCl_3$ $CCl_4 + CO_2$ (Hentschel, J. pr. Chem. 1877, 306)

The technical preparation of carbon tetrachloride is generally carried out by the direct chlorination of carbon disulphide in the presence of powdered aluminium chloride, the quantity of catalyst necessary being only about 1 p.c. of the carbon disulphide used.

$$CS_2 + 3Cl_2 \quad CCl_4 + S_2Cl_2$$

The sulphur chloride reacts separately with more carbon disulphide in the presence of iron filings, and the crystalline sulphur which is formed is employed again in the manufacture of carbon disulphide (Urbain, Chem. Zeit. 1902, 1086 ; Breteau, J. Pharm. Chim. 1908, 110 ; Urbain, J. Soc. Chem. Ind. 1902, 926 ; Eng. Pat. 13733).

Later modifications of the process consist in the further chlorination of the sulphur monochloride, in the presence of antimony chloride, before treatment with carbon disulphide (Haworth and Baker, J. Soc. Chem. Ind 1906, 559), and the use of a solution of sulphur in sulphur monochloride, in a finely divided condition, as a chlorine carrier (Acker and Struc, *ibid.* 1908, 833). Instead of aluminium chloride, aluminium amalgam has been employed (Castner Co. *ibid.* 1905, 903). Under this patent, the resulting carbon tetrachloride is purified by treatment with a solution of alkaline sulphide containing free alkali, the carbon disulphide being removed as thiocarbonate (*cf.* Dow Chemical Co. U.S. Pat. 1204608 ; J. Soc. Chem. Ind. 1916, 35, 1271).

The Isco Chemical Co. (U.S. Pats. 1260621 and 1260622) treat carbon disulphide containing free sulphur with chlorine in presence of a catalyst to form sulphur dichloride and carbon tetrachloride, and an additional quantity of carbon disulphide is then added to convert the sulphur dichloride into sulphur monochloride,

with the formation of more carbon tetrachloride. The product is treated with sufficient tin to convert the sulphur monochloride into sulphur, with the formation of stannic chloride, and after separating the sulphur, water is added to hydrate the stannic chloride, and the carbon tetrachloride is recovered from the mixture by distillation.

A number of electric-heating processes have been suggested. A mixture of sodium chloride and silica is heated in the lowest portion of a furnace lined with magnesia, and provided with three sets of electrodes, one above the other. The middle electrodes heat a mass of coke, and the chlorine from the alkali chloride reacts with the incandescent carbon, forming carbon tetrachloride, which, after passing through the arcs between the third set of electrodes, is distilled off. The temperature does not exceed 2000° (Machalske and Lyon, J. Soc. Chem. Ind. 1903, 1298 ; Machalske, Chem. Zentr. 1904, 1, 1069). The chlorine can also be supplied from an external source, the carbon only being heated by electricity (Maywald, J. Soc. Chem. Ind 1907, 1253).

Another process consists in heating together lime, calcium chloride, and carbon in the absence of air in an electric furnace, in the proportions indicated by the equation

$$2CaO + 2CaCl_2 + 10C = 4CaC_2 + 2COCl_2$$
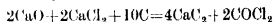
The carbonyl chloride is led over heated coke, animal charcoal, or pumice, where it is decomposed into carbon tetrachloride and carbon dioxide by surface contact (Machalske and Darlington, J. Soc. Chem. Ind. 1906, 559).

A mixture of calcium chloride and coke, heated in the electric furnace in a stream of chlorine, also yields carbon tetrachloride (Matthews and Darlington, *ibid.* 1906, 1232).

The halogenation of metallic or other carbides, such as acetylene, also yields carbon halides, so long as the temperature is kept below the dissociation point of the halide required (Blackmore, *ibid.* 1908, 712).

Carbon tetrachloride is a transparent colourless liquid, with a pungent aromatic odour ; m.p $-22.7°$; b.p $76.74°$; and sp.gr. 1.63195, $0°/4°$ (Thorpe, Chem. Soc. Trans. 1880, 201) ; $76.96°$ (corr.) (Thorpe and Rodger) ; (Moles, Anal. Fis. Quim. 1912, 10, 30). Its specific heat increases regularly from 0.2010 at $0°$ to 0.2031 at $70°$. The specific heat of the vapour falls from 0.14 at $0°$ to 0.115 at $70°$ (Mills and MacRae, J. Physical Chem. 1911, 15, 54).

The vapour pressure of carbon tetrachloride has been measured by Schreinemakers (Zeitsch. physikal. Chem. 1904, 48, 445). The compressibility has been measured by Richards and Stull (Amer. Chem. J. 1904, 26, 408). In the solid state carbon tetrachloride is trimorphous, the three modifications melting at $-28.6°$, $-23.77°$, and $-21.2°$ respectively, the second being the form usually obtained (Tammann, W. Ann. 1898, 489). The refractive index for the line F is 1.4726, and for the line D is 1.4658 (Gladstone, Chem. Soc. Trans. 1886, 623).

Its dielectric constant has been measured by Turner (Zeitsch. physikal. Chem. 1900, 385), Drude (Zeitsch. physikal. Chem. 23, 267), and Veley (Phil. Mag. [6] 11, 73). Its solubility in water, which is extremely small,

has been measured by Rex (Zeitsch. physikal. Chem. 55, 355).

It is *soluble* in alcohol and ether, and *dissolves* a large number of organic substances, especially those of a fatty nature, whence its wide application in the arts. It is preferable to carbon disulphide on account of its non-inflammability. With sulphonated oils and resins it yields a gelatinous soap, which is miscible with water (Stockhausen, Chem. Zentr. 1906, ii. 731). It yields chlorine and lower chlorides of carbon on passing through a red-hot tube (Regnault, *l.c.*). When mixed with hydrogen and passed through a red-hot tube with pumice, it yields marsh gas and ethylene (Berthelot, Ann. Chim Phys. 1858, 53, 69).

The same mixture passed over reduced nickel yields hexachlorethane (carbon trichloride) at 270°. With excess of hydrogen at the same temperature, tetrachlorethylene (carbon dichloride) is obtained (Sabatier and Mailhe, Compt. rend. 1904, 138, 407).

Mixed with sulphuretted hydrogen and passed through a red-hot tube, the vapour of carbon tetrachloride yields hydrochloric acid and carbon sulphochloride $CSCl_2$ (Kolbe, Annalen, 1843, 45, 41, and 1845, 54, 146).

Heated under pressure with oxygen and water at 250°, it forms carbonyl chloride and carbon dioxide (Goldschmidt, Ber. 1881, [14] 928). In alcoholic solution, and treated with potassium amalgam, it yields chloroform, marsh gas, and methylene chloride (Regnault, *l.c.*). Phosphorus pentoxide at 200° acts in two ways: in the first, carbonyl chloride and carbon dioxide are produced; in the second, in the presence of more phosphorus pentoxide, carbon dioxide alone is obtained.

$$2CCl_4 + P_2O_5 = COCl_2 + CO_2 + 2POCl_3$$
$$3CCl_4 + 2P_2O_5 = 3CO_2 + 4POCl_3$$
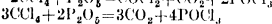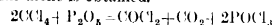
(Gustavson, Zeitsch f. Chem. 1871, 615)

A similar reaction takes place at 100° with sulphur trioxide, carbonyl chloride being formed:

$$CCl_4 + 2SO_3 = S_2Cl_2O_5 + COCl_2$$
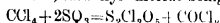
(Erdmann, Ber. 1893, 26, 1993).

With the oxides of many metals, a similar production of carbonyl chloride, together with carbon dioxide and the chloride of the metal, takes place (Demarcay, Compt. rend. 1887, 104, 111 ; Quantin, *ibid.* 1887, 104, 223 ; 1888, 106, 1074 ; Delafontaine and Lineberger, Amer. Chem. J. 1896, 532).

With zinc and dilute acid, carbon tetrachloride is converted into hydrochloric acid and chloroform (Geuther, *l.c.*). Alcoholic potash slowly converts it into potassium chloride and carbonate (Regnault, *l.c.*). By long-continued action at 100° in sealed tubes, alcoholic potash converts it partially into ethylene (Berthelot, Ann. Chim. Phys. 1859, 109, 118). With alcoholic potash and aniline it yields phenyl*iso*cyanide (*cf. Chloroform*). With phenylamine it yields di-phenylaminobenzamide (Hofmann, Proc. Roy. Soc. 9, 284, and 10, 184 ; Wieth, Ber. 1877, 10, 358 ; Michler and Walder, Ber. 1881, 14, 2171), a reaction facilitated in presence of a copper-mercury couple (Hartung, Chem. Soc. Trans. 1918, 113, 163). By the action of sulphur at 220°, a number of sulphochlorides of carbon are formed, the final product being carbon disulphide (Klason, Ber. 1887, 20, 2376). It is

decomposed at 200° by molecular silver, being converted into hexachlorethane C_2Cl_6 (Goldschmidt, Ber. 1881, 14, 927). By heating with aluminium bromide it is readily converted into carbon tetrabromide (Gustavson, Bull. Soc. chim. 1881, 556).

Heated in a sealed tube for 10 hours at 130° with hydriodic acid, carbon tetrachloride yields iodoform and hydrochloric acid (Walfisz, *ibid.* 1893, 7, 256). Acetylene reacts with carbon tetrachloride, yielding free carbon in a very finely divided form, hydrochloric acid being formed at the same time (Sandman, Chem. Soc. Abstr. 1902, 82, i. 581). Carbon tetrachloride reacts with benzene in the presence of aluminium trichloride, giving, as chief product, diphenyl-dichloromethane, $CCl_2(C_6H_5)_2$ (Boeseken, Chem. Soc. Abstr 94, i. 189). Carbon tetrachloride absorbs ozone, giving a blue solution.

In its physiological action, carbon tetra-chloride strongly resembles chloroform.

Its popularity as a solvent in the arts has been somewhat diminished by the increasing manufacture of tetrachlorethane $C_2Cl_4H_2$, as the latter is more indifferent toward metals, and is readily produced by the action of chlorine on a double compound of antimony pentachloride and acetylene (D. R. P. 154657, 1906).

Carbon trichloride, *Carbon hexachloride, Tetrachlorethylene dichloride, Hexachlorethane, Perchlorethane* C_2Cl_6, discovered by Faraday (Phil. Trans. 1821, 47), also investigated by Regnault (Ann. Chim. Phys. 1838, [2] 69, 166, and 1839, [2] 71, 371). Is obtained by the action of chlorine in sunshine upon various derivatives of ethyl and ethylene, on carbon dichloride ; on ethylene chloride (Faraday, *l.c.*) ; and also (Liebig, Annalen, 1, 219) on ethyl chloride, first in the shade, afterwards in sunshine (Laurent, Ann. Chim. Phys 1837, [2] 64, 328), on mono-, di-, or tri-chlorinated ethyl chloride (Regnault, *l.c.*) ; on ethyl sulphite (Ebelmen and Bouquet, *ibid.* 1846, [3] 17, 66), on ethyl oxide (Regnault) ; on hydrochloride of ethylamine (Geuther and Hofacker, Annalen, 1858, 108, 51) (in this process some chloride of nitrogen is produced) ; by passing the tetrachloride through a red hot tube (Kolbe, Annalen, 1845, 54, 147) ; by distilling perchlorethylic oxide, and repeatedly treating the distillate with water (Malaguti, Ann. Chim. Phys. 1846, [3] 16, 14) ; by heating carbon tetrachloride with copper powder at 120° (Radziszewski, Ber. 1887, 17, 834) or with molecular silver at 200° (Goldschmidt, *ibid.* 1881, 14, 928) ; by heating acetyl chloride with excess of phosphorus pentachloride at 180° (Hubner and Muller, Zeitsch. f. Chem. 1870, 328) ; by heating propyl chloride or *iso*-butyl chloride with iodine trichloride at 200° (Krafft and Merz, Ber. 1875, 8, 1298) ; by treating pentachlorethylchloroformic ester with aluminium chloride (Müller, Annalen, 1890, 258, 63).

Carbon trichloride crystallises from a mixture of alcohol and ether in right rhombic prisms (Gossner, Chem. Zentr. 1903, ii. 1052). Colourless, transparent, and nearly tasteless, but having an aromatic odour resembling that of camphor ; sp.gr. 2·0 ; m.p. 184°–186° (Bolton, Zeitsch. Elektrochem. 1902, 8, 165 ; 1903, 9, 209), volatilising even at ordinary temperatures ; b.p. 185° (Hahn, Ber. 1878, 11, 1735). Insoluble in water; soluble in alcohol and ether,

and in all oils. Converted, by repeated distillation, into the dichloride and free chlorine. Burns with a red light in the flame of a spirit lamp. Mixed wth hydrogen and passed through a red-hot tube, it yields dichloride and hydrochloric acid (Geuther, *l.c.*). Metals heated in its vapour form metallic chlorides, carbon being deposited. Heated in sealed tubes with potassium hydroxide, it yields potassium oxalate and chloride

$$C_2Cl_6 + 8KHO = K_2C_2O_4 + 6KCl + 4H_2O$$
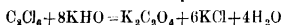
(Geuther, J. 1859, 277). The same products together with hydrogen and ethylene are formed when it is heated with alcoholic potash in sealed tubes (Berthelot, Annalen, 1859, 109, 118).

Reducing agents such as zinc and dilute sulphuric acid, or alcoholic potassium hydrogen sulphide (Regnault, *l.c.*), reduce it to tetrachlorethylene (carbon dichloride). The same reaction takes place when it is heated with silver at 280°. Sulphur trioxide acts upon it at 150° according to the equation

$$CCl_3 \cdot CCl_3 + 2SO_3 = CCl_3 \cdot COCl + S_2O_5Cl_2$$
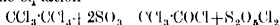
(Prudhomme, Annalen, 1870, 156, 342).

Carbon dichloride, *Tetrachlorethylene* C_2Cl_4 (Faraday, Phil. Trans. 1821, 47; Regnault, Ann. Chim Phys. 1839, [2] 70; [2] 71, 372), is formed as a liquid coloured with chlorine when the vapour of carbon trichloride is passed through a red-hot tube filled with fragments of glass. It is purified by passing it repeatedly through a red-hot tube, then shaking up with mercury and rectifying at a low temperature (Faraday). More easily obtained by adding carbon trichloride in small portions to an alcoholic solution of hydrogen potassium sulphide, as long as sulphuretted hydrogen is given off. The liquid is distilled and carbon dichloride separates from the distillate on dilution with water (Regnault, *l.c.*); or by reduction of carbon trichloride with zinc and sulphuric acid. Mobile liquid of sp.gr 1 619 at 20° (Regnault), 1·612 at 10° (Geuther); b.p. 122° (Regnault), 116° (Geuther); 120·74° (corr.); sp gr. 1·6551 0°/4° (Thorpe and Rodger); remains liquid at − 18°, and does not conduct electricity. Insoluble in water, acids, and alkalis, but dissolves in alcohol and ether, and oils. Decomposed at a red heat into the *hexaclorobenzene* C_6Cl_6 and free chlorine. When its vapour is passed over baryta at a red heat, it is decomposed with vivid ignition into barium chloride, carbon dioxide, and charcoal. It absorbs bromine in the sunshine, forming *carbon chlorobromide* $C_2Cl_4Br_2$. It is converted by continued heating to 200° with potassium hydroxide into potassium oxalate and chloride, hydrogen being given off (Geuther, Annalen, 247). It absorbs dry chlorine in sunshine, forming the trichloride, but is converted into *trichloracetic acid* when exposed to an atmosphere of chlorine under water

$$C_2Cl_4 + 2H_2O + Cl_2 = 3HCl + C_2HCl_3O_2$$

(Kolbe, Annalen, 1845, 54, 181).

as-**Heptachloropropane** C_3Cl_{10}, a crystalline substance, m.p. 32°, formed by the action of phosphorus pentachloride on pentachloroacetone; also obtained by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride (Böeseken and Prins).

Hexchlorobenzene C_6Cl_6; m.p. 225°; discovered in 1821 by Julin and investigated by Phillips and Faraday (Phil. Trans. 1821), and by Regnault (Ann. Chim. Phys. [2] 70, 144), who prepared it by passing the vapour of chloroform or tetrachlorethylene through a porcelain tube filled with fragments of porcelain and heated to redness. Obtained from methylene chloride by 1Cl or 1Cl₃ (Höland, Annalen, 240, 234); the crystalline product is dissolved in ether, filtered, evaporated to dryness, and sublimed. Obtained by Hugo Müller as a final product of the action of antimony pentachloride or chlorine in presence of iodine on benzene. It is also obtained by sending a current of 5 5 amperes and 42 volts for ⅓ hour between carbon electrodes in an atmosphere of chlorine. If a higher current and voltage are used, and it is continued for much longer, the trichloride C_2Cl_6 is formed. Bromine yields similar compounds (Bolton, *l.c.*). Forms white delicate needles with a silky lustre, tasteless, but with an odour resembling spermaceti; sublimes without fusion at 120°.

Insoluble in water, acids, and alkalis, but soluble in alcohol, ether, and hot oil of turpentine. Decomposed into chlorine and charcoal on passing through a red-hot porcelain tube filled with glass or rock crystal. Burns with a bluish colour in the flame. Potassium burns on being strongly heated in its vapour. Formerly regarded as carbon monochloride: molecular formula established by Bassett (Chem. Soc. Trans. [2] 5, 443).

Carbon tetraiodide, *Tetraiodomethane* CI_4. Dark-red octahedra; sp.gr. 4·32; obtained by action of aluminium iodide on a mixture of carbon tetrachloride and disulphide (Gustavson, Ber. 14, 1705). For other methods, *see* Spindler, Annalen, 231, 257; Moissan, Compt. rend. 113, 19; Robineau and Rollin, Chem. Centr. 1894, i. 1140; Lantenois, Compt. rend. 1913, 156, 1385.

Carbon nitride (*v.* *Cyanogen,* art. CYANIDES).

Carbon subnitride C_4N_2 has been obtained by Moureu and Bongrand (Compt. rend. 1910, 150, 225) by removing two molecules of water from the diamide of acetylene dicarboxylic acid. $CONH_2 \cdot C : C \cdot CONH_2 = N : C \cdot C : C \cdot C : N + 2H_2O$. It forms fine white needles; m.p. 20·5°–21°; b.p. 76° at 753 mm., and its vapour has an odour and an irritating action resembling that of cyanogen. It is readily combustible, takes fire spontaneously at 130°, burning with a purple flame, also resembling that of cyanogen. It has an abnormally high molecular refraction and dispersion, and a density of 0·9703 at 25°/4°. For its behaviour towards ammonia and amines, *see* Moureu and Bongrand, Compt. rend. 1914, 158, 1092.

Carbon oxychloride $COCl_2$, *Carbonyl dichloride, Chlorocarbonic acid, Phosgene gas.* First obtained by J. Davy by action of sunlight on mixture of carbon monoxide and chlorine. (For details of this mode of preparing it, *v.* Emmeling and Lengyel, Annalen Suppl. 7, 101, and Wilm and Wischin, *ibid.* 147, 450.) By passing the gases over heated animal charcoal combination occurs in the dark. Also obtained by passing carbon monoxide into boiling antimony pentachloride (Hofmann, *ibid.* 70, 129; Butlerow, Zeitsch. f. Chem. 1863, 484; Kraut,

Gm.-K. 1 2, 380); by heating carbon tetra-chloride with zinc oxide in closed tubes at 200°, or by mutual action of carbon tetrachloride and carbon monoxide at 400° ; or by heating a mixture of chloroform, potassium dichromate, and sulphuric acid (cf. Plotnikow, J. Russ. Phys. Chem. Soc. 1916, 48, 457).

Carbon oxychloride is a colourless liquid, boiling at 8·2°, and of sp.gr. 1·432 0/4°. Soluble in acetic acid and benzene ; decomposed by water: $COCl_2 + H_2O = CO_2 + 2HCl$. With alcohol forms *chlorocarbonic ester* Cl·COOC$_2$H$_5$. Combines with ammonia to form *urea* and ammonium chloride. With aniline it forms diphenylurea. Its presence in may be detected by this reaction (Kling and Schmutz, Compt. rend. 1919, 168, 773).

Carbonyl cyanide CO(CN)$_2$ is a yellow amorphous non-volatile solid, formed by subjecting a mixture of carbon monoxide and cyanogen to the ultra-violet rays from a mercury-quartz lamp. It dissolves in alkalis, forming a yellow solution, and slowly hydrolyses on the addition of acid, giving carbon dioxide and hydrogen cyanide (D. Berthelot and Gaudechon, Compt. rend 1913, 156, 1766).

Carbon disulphide. *Thiocarbonic anhydride, Sulphocarbonic acid* CS$_2$. This compound was discovered by Lampadius, in 1796, by heating pyrites with charcoal Clement and Desormes, in 1802, in examining the action of sulphur on red-hot charcoal, obtained the same product. Its nature was established by Vauquelin.

Manufacture.—Schrotter in Germany, and Peroncel in France, first prepared carbon disulphide on a manufacturing scale. Schrotter employed a cylinder of Hessian clay in which the charcoal was heated ; the sulphur was introduced through a hole near the bottom, to the upper end was fixed an exit tube for the vapour of the carbon disulphide formed. The apparatus produced about 20 kilos. of the disulphide in 12 hours.

Deiss and Fisher employed cast-iron cylinders in which the vapour of sulphur passed over charcoal heated to redness. Fireclay retorts glazed internally to prevent the escape of vapour through the pores were also used, each cylinder was about 5 feet high and nearly 20 inches diameter. Four retorts were arranged in a single furnace in such a way that the flame of the fire could play entirely round them. Each retort was divided internally into two parts by means of a perforated shelf ; the upper compartment, which was the larger of the two, served to contain the charcoal, which could be thrown in through a special opening in the lid without interrupting the working. A second opening in the top of the retort was provided with a tube about 2 inches in diameter, which led directly into the lower compartment, and was used to throw in sulphur as required. The vapour of carbon disulphide which was formed during the process was conducted through a delivery pipe connected with a third opening in the retort into the condensers. The four retorts, having been filled with charcoal and the lids closed, were heated to redness by a coal fire. Pieces of sulphur wrapped in cylindrical paper packets were then dropped in the pipes leading to the lower partitions of the retorts. Two such packets, each containing about 5½ oz. of sulphur, were thrown in at intervals of about 3 minutes, the opening at the end of each tube being closed at each successive addition. The charcoal was renewed every 7 hours, and was heated about an hour and three-quarters each time before the necessary temperature was attained for its combination with sulphur. The vapour of carbon disulphide mixed with that of sulphur escaped through the delivery tubes, passing into the first row of condensers, where it was partially condensed, together with some sulphur ; the undissolved sulphur was recovered and used over again. The uncondensed vapours passed on into the second row of condensers, and so on till the last row. The condensers, amounting to 18 or 20 in all, were connected together by pipes, the last of which was connected with the chimney of the works, or better, with vessels or tubes containing layers of pulverised lime to absorb the sulphuretted hydrogen which would otherwise create a nuisance in the neighbourhood of the factory.

The condensers were made of sheet zinc, were cylindrical in shape and about 26 inches in diameter, bottomless, with slotted sides, and stood in a kind of shallow cistern containing water a little deeper than the openings, so as to form a water lute, permitting the passage of the condensed liquid while closing the exit against vapours. The lids of these condensers were furnished with rims forming a kind of saucer, containing water to assist in the condensation of the vapour. Each lid had two openings in the form of tubulures, into which the pipes were fixed for the transmission of the vapours from condenser to condenser.

Gérard employed a vessel of cast iron 6½ feet in height, about 4 feet 8 inches in diameter, and sides 1¾ inch thick (Fig. 15). The retort was elliptical
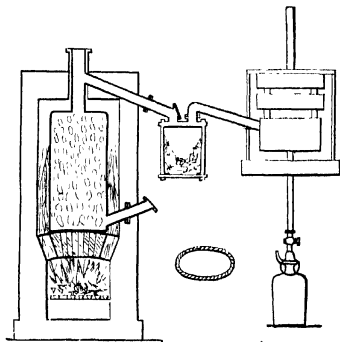

FIG. 15.

in section, stood upon a brickwork arch, and was heated from below by a fire. Near the bottom was a pipe fitted with a valve, through which sulphur could be introduced into the cylinder. At the upper extremity was a wide pipe which could be closed with a lid, and served for the introduction of charcoal into the apparatus. Another pipe, cast in one piece with the upper one, sloped forward and passed into a receiver in which the sulphur which passed over during the

operation was condensed, and could be easily removed by opening a valve in a tubulus placed at a bend in the pipe ; the more volatile carbon disulphide passed forward into the condensers. The condenser consisted of three vessels, cylindrical in form, arranged one above the other, and communicating by vertical pipes. The topmost condenser had an exit pipe for sulphuretted hydrogen, &c., and the condensed carbon disulphide could be drawn off into a receiving vessel beneath by opening a cock in a pipe proceeding from the lower condenser.

The three condensers were contained in a tank 5 feet high and 5 feet wide, filled with water, which could be renewed at pleasure.

The sulphur was added in portions of about 3 lbs. at intervals of 3 minutes. The oven was heated during the night to volatilise the sulphur, and the residual charcoal was added to the new charge. This apparatus yielded in 24 hours about 570 lbs. of carbon disulphide, consisting theoretically of 480 lbs. of sulphur and 90 lbs. of carbon ; in practice 530 lbs. of sulphur and 242 lbs. of wood charcoal were used. Gérard found it advantageous to surround the generating vessels with brickwork, which rendered them more durable.

Only retorts of a certain size could be employed, as, when they were too large, the heating was irregular, causing waste of sulphur. When using unrefined sulphur, the retorts needed cleaning every fortnight, but with purified sulphur they could be kept working for two months.

The present mode of manufacture is thus described by Ignatius Singer (J. Soc. Chem. Ind. 8, 1889, 83) (see Fig. 16) :

A is a vertical cast-iron retort, or, better still, made of earthenware, glazed inside, of elliptical shape, about 66 inches high, and 20 by 12 inches internal diameter. It rests on a support, B, made of firebricks, and is protected by a mantle of best firebricks, C, about 4 inches thick, leaving a space of from ½ to ¾ inch between it and the retort. The metal of the retort should not be less than 2 inches in thickness. D is the outer brickwork of the furnace lined on the inside with firebricks, D'; E, E, fire-grates ; E', ash pits ; F, furnace doors, made of frames, a, into which a fire-proof slab, b, is inserted. The
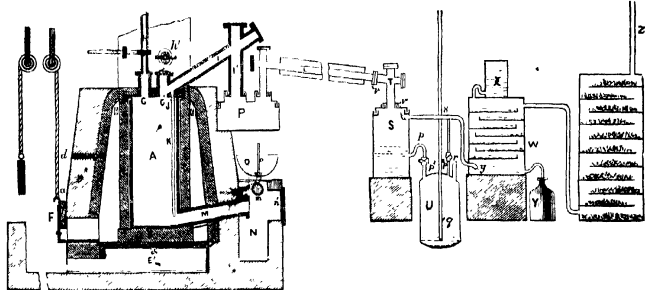
FIG. 16.

furnace doors are suspended by cables running over pulleys, and are counterpoised, so that they can be raised or lowered. At d is shown a small peep-hole, through which the temperature in the furnace may be watched. In the lid of the retort are cast two tubes, G and G', of about 5 inches internal diameter and not less than 1 inch in thickness, but it is advisable to have them made somewhat stronger, as the lid will then outlast several retorts. Over the openings, G, a vent-pipe or flue, H, is suspended by a lever, so that it can be raised or lowered at will, one end of which passes through the roof. When fresh charges of charcoal are to be introduced into the generator A, which is done through the tubulure G', the lid closing the tube G is first removed, and the vent-pipe H quickly lowered, which serves the purpose of carrying off the noxious gases that would otherwise be injurious to the workmen. G' may now be opened, and the carbon fed in without the slightest inconvenience.*

From the tubulure G' issues a pipe, I, inclined upwards, through which the disulphide of carbon vapours escape. Most of the free sulphur passing over will condense here and run back into the retort. But the partially cooled sulphur

falling on to the surface of the incandescent carbon would be immediately vapourised again, at the same time cooling down the top layer of the charcoal. To obviate this, Singer suggests that an opening should be made in the lower part of the pipe I, to which a hopper can be fitted, as shown at J, terminating in an earthenware pipe K, reaching nearly to the bottom of the retort. By this means the sulphur distilling over uncombined would be conducted back to the bottom of the generator, the pipes would be less liable to be choked up, while the resulting product would be purer.

From the lower end of the retort, close to the bottom, a pipe M branches off, a little upwards inclined, passing through the brickwork and terminating in a chamber N, with door n. During work this pipe is carefully closed by a lid. It serves the purpose of raking the ashes out of the retort, which is done once a week. At m a flue is shown, carrying the noxious gases into the chimney. The ashes are allowed to cool here before their removal. Adjoining this chamber is a hearth into which an iron vessel, O, is fitted, for melting the sulphur. It is heated by a flue from the furnace passing underneath it, provided with a damper

to regulate the heat. (In Fig. 16 this sulphur vessel is raised so as to make it visible in the drawing.) A pipe, o', closed by a conical valve to which an iron rod, o, is attached, connects the sulphur pot with the arm M of the retort, by which means the sulphur can conveniently be introduced into the latter.

The sulphur flowing down the incline of the arm M arrives at the bottom of the retort, where it is volatilised: the vapours, passing upwards, combine with the carbon. The generated disulphide vapours escape through pipe I, and then pass down the vertical tube I' into a vessel P, where any excess of sulphur is deposited. The lid of this vessel rests in hydraulic seals, and is connected with the inlet and outlet pipes by a kind of telescopic tube made air-tight by water. When the vessel P is to be removed, the lid is raised, the vessel taken away, another similar one put in its place, and the lid lowered again. This should be done once a week only, and never while distillation is going on.

The carbon disulphide vapours, now freed from the greater part of uncombined sulphur, pass through a Liebig's condenser, L, about 30 feet long, into a receiver, S, partially filled with water. The crosspiece T, connecting the Liebig's condenser with the receiver, is made so that it can be detached—being secured at v by flanges bolted together, and at v' by water seal—for purposes of cleaning, &c. From here the disulphide is allowed to run through a siphon, p, direct to the storage tanks. A better plan, however, is to keep the storage tanks for the crude product on a high level, which greatly facilitates the after-process of purification. In this case the disulphide of carbon is allowed to flow into a *montejus*, U, as shown in drawing. A pipe q, reaching nearly to the bottom, is passed through the cover of the *montejus* to the high-level tank. A second pipe, r, connects the vessel U with a force-pump. On air being pumped into U through r, the stop-cocks p' and p' having been shut off, the disulphide is pressed up through pipe q into the tank. This is a far better method than using pumps, as in the latter it is difficult to prevent leakage, the crude disulphide having a very corrosive action on most metals. For the same reason, the receivers, tanks, &c., for the crude substance should all be lined with sheet-lead, as wrought-iron vessels soon perish, while copper is even more energetically acted upon. Cast iron withstands corrosion much better, but is objectionable on account of its porosity. This might be remedied, however, by giving the vessels repeated coatings of dilute silicate of soda, both inside and outside, the vessels being first slightly heated with steam and the silicate applied while warm.

Near to the top of the receiver S is a pipe, s, for carrying off the uncondensable vapours—chiefly sulphuretted hydrogen. The gases are conducted into a rectangular vessel, W, where they are made to circulate in zigzag over a series of shallow trays filled with a vegetable oil, to absorb any disulphide vapours which have escaped condensation. The oil can be made to trickle from a reservoir, x, as shown, through a goose-necked pipe, which, passing from tray to tray in an opposite course to that of the gases, finally trickles through x into a receiver Y. When a sufficient quantity has accumulated here, the

disulphide is distilled off and the oil returned to z. Before the gases enter this absorber they are 'washed' by making the end of the pipe s dip into the oil as shown at y whereby the apparatus is disconnected from contact with air. The gases are now passed through a second vessel, Z, similar in construction to the one just described, only substituting lime or oxide of iron for the oil, to absorb the H_2S, and are then allowed to escape into the open air through the pipe z.

Above the retort A, and between it and the chimney, set at right angles to each other, is a smaller retort, similar in construction to A, but only about one-third the capacity of the latter, and is heated by causing the products of combustion coming from the furnace to circulate round it before finally passing into the chimney. (Only the discharge hole h', corresponding to the arm m of the retort A, is visible in the drawing.) As the generator A requires fresh charges of carbon every 8 hours, it is very economical to keep this small retort always filled with charcoal, which by the time it is required will be red hot, and no more time need be lost than is required for transferring it from the one into the other retort. By this arrangement, part of what would otherwise be waste heat is utilised, and a great saving in time and fuel effected. A still better plan is to make the charcoal on the spot, 8 hours being more than sufficient to char the wood and to heat it up to bright redness. Spent dyewoods, tanner's refuse, or sawdust, are excellent for the purpose, and as these would not require crushing—as when charcoal is bought in lumps—a saving in labour, possibly also in money, might be made, besides being more cleanly. By a small outlay, the vapours might be condensed, and pyroligneous acid obtained as a by-product.

The apparatus is worked as follows: After having allowed the brickwork to set and partially dry for a few days, the fires are started, at first gently, to prevent the brickwork from cracking, then gradually increasing the heat until the retort becomes a dull-red colour. The latter is now filled with small charcoal, and the smaller retort with chips, sawdust, &c., and the fires are now urged until the retort and the charcoal in it have become a 'cherry red.' This heat should never be exceeded, nor should it be allowed to fall below this, as in either case it would result in a lesser yield of carbon disulphide.

When the proper temperature is attained, the two openings in the lid of the retort are closed, the lids being screwed down tightly, with some clay made into a thick paste as a lute. A better way would be to cast in the top of these tubulures grooves, and the lids with a rim loosely fitting into these grooves, forming what is called an hydraulic seal, only using lead in the place of water. The heat here is sufficient to melt lead, but not so great as to prevent its use. This would form a much better lute, and could be opened and closed in much less time, which, in the case of disulphide of carbon manufacture, is a great desideratum. Having previously secured all the joints throughout the apparatus, sulphur is now run in by raising the rod o' in the sulphur pot. A bubbling will immediately be heard in the gas washer at y, caused by the escape of sulphuretted hydrogen, &c. In a few minutes, this bubbling ceases, and carbon disulphide

begins to distil over. Distillation is now proceeding, sulphur being charged in every 5 minutes, about 1¼ to 1¾ lbs. each time, for 7 hours, when the supply of sulphur is stopped, and one hour allowed to elapse before fresh charcoal is filled in. The lid is then removed from c, and the flue-pipe H lowered. c' may now be opened, and last of all the lid h' is removed from h of the carboniser, and the red-hot charcoal raked from the carboniser, by means of a funnel or hopper, into the retort A. The retort is now closed, taking care that the opening communicating with the flue H is the last to be shut off, and work started again. At the end of each week, neither coal nor sulphur is charged in for 8 hours, after which the whole apparatus is cleaned out in the following manner : The flue H having been lowered on to G as described above, the cover at the end of the delivery pipe I is removed, and wet bags or pieces of canvas are tightly rammed down the pipe I, and past its junction with the vertical pipe I', so as to isolate the condensers, &c., from the furnace. The ashes are now raked out through M, as described above, the retort refilled with fresh charcoal, and while this is getting heated up, the other portions of the apparatus are examined, and where sulphur is present it is removed.

With one such retort, from 4 to 5 cwts. of carbon disulphide can be made in a day, but it is much more economical, both in labour and fuel, to have several retorts—say four—in the same furnace.

MANUFACTURE OF CARBON DISULPHIDE BY THE ELECTRIC FURNACE.

Carbon disulphide is now made on the large scale, near Penn Yan, N.Y., America, by the Taylor Chemical Company, by means of an electric furnace, devised and patented by Mr. Edward R. Taylor (U.S. Pat. 688364, Dec 10, 1901 ; 871971, Nov. 26, 1907), who has kindly supplied the information upon which the following description of the process is based. The construction of the furnace is shown in Figs. 17, 18, 19, 20, 21. Fig. 17 shows a section in elevation through the electrodes, and Fig. 18, shows a cross section in elevation at right angles, the figures being taken from the patent specifications. In Fig. 17 is shown the position of the electrodes d, D, near the bottom of the furnace shaft, which is represented as filled with charcoal ; in Fig. 18, they are seen at d. At k (Fig. 17) are pipes through which are passed broken carbons, i.e. refuse from the factories of carbons for arc lights, for the purpose of reinforcing the main carbons ; these pass down, upon, and over the ends of the main carbons, and convey the current from the electrodes to the charcoal. The intermediate conductive material protects the electrodes proper from the intense heat and eroding action and thereby prolongs their life. It also tends to steady the current, fluctuations being mainly due to variations in power and not to changes of resistance in the furnace itself. The charcoal for the reaction is fed into the furnace through the opening x (Fig. 17). Preferably four electrodes are used in this construction, supplied with two-phase alternating current. Provision is made for keeping the metallic portions of them comparatively cool by feeding cold sulphur on to them through the inlets shown as v (Fig. 17), and

which can be replenished through the hoppers n, the sulphur passing into the annular chambers

FIG. 19.
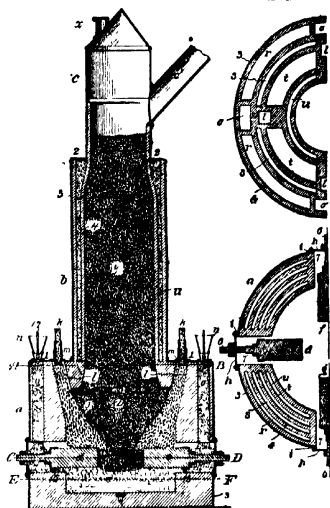
FIG. 17.   FIG. 20.

shown below the hoppers, seen in detail in Figs. 19, 20, and 21. The interior of the furnace thus filled with sulphur, which is gradually melted and finds its way to the reaction zone. By this construction, the heat that would otherwise be radiated from the external walls of
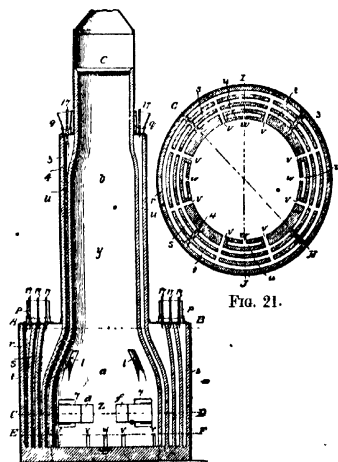

FIG. 21.

FIG. 18.

the furnace is absorbed, and no outside lagging is needed. The furnace is 16 feet in diameter

and 41 feet high. It needs much less care and is easier to manage than one of the small iron or clay retorts generally used.

In working, charcoal is put into the charger above the bell and the opening sealed. The charcoal falls into the shaft of the furnace as often as there is room for it, the charger being replenished from time to time. The shaft should be kept filled with charcoal and the internal spaces filled with sulphur: thus there is no loss of heat by radiation and the heat

charge. The sulphur within the working chamber z soon becomes melted, and its level rises more or less nearly to the top of the electrodes. As it approaches the heat zone, the sulphur is vapourised and rises through the charcoal which, when sufficiently heated, combines with it, forming the disulphide, the vapour of which ascends through the charcoal

FIG. 22.

FIG. 23.
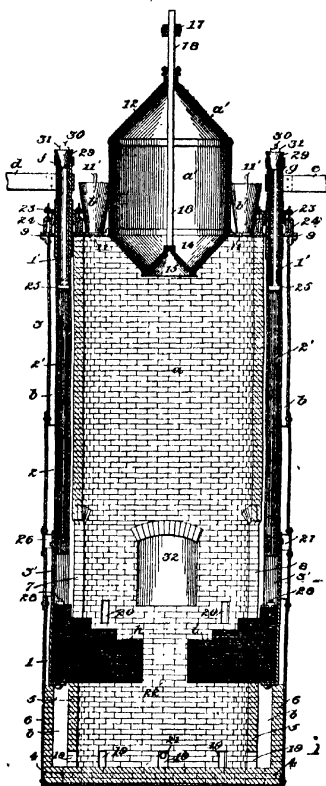
absorbed in melting the sulphur is returned to the furnace.

Electricity is supplied in such quantity that the electrodes are not submerged in the melted sulphur to such an extent as to restrict the passage of the current. The electricity is ordinarily passed from the one electrode to the other immediately opposite, but the direction can be changed at any time so as to pass to the adjacent electrode, thus burning out any piers or ' scaffolds ' that may form in the corners and which would prevent the regular descent of the
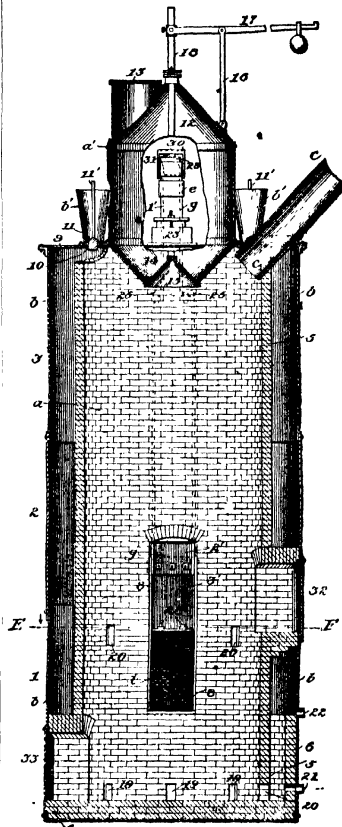
in the shaft, and passes out through the pipe x. to a condenser. The furnaces are run for about a year before renewing the electrodes or cleaning out. Aluminium bars, 6 inches wide and ⅝ inch thick, connect the insulated electrodes with two Stanley inductive type dynamos, each of 330 kilowatts capacity, run, as a rule, by water power. The average voltage is about 50. The yield is usually about 14,000 lbs. of the disulphide in 24 hours, but it is capable of being increased to 25,000 lbs.

An improved type of electric furnace, more

particularly adapted for a smaller installation, is seen in Figs. 22 and 23, reproduced from the patent specifications.

Fig. 22 shows the furnace in sectional elevation. Fig. 23 shows a sectional elevation with the plane of the section at right angles to that of Fig. 22, and with portions broken away at top to expose parts behind the plane of the section. Fig. 24 is a top view on which the planes of Figs. 22 and 23 respectively are indicated by broken lines, A–B and C–D; and Fig. 25 represents a horizontal section on the line E F (Fig. 23). Like reference characters refer to like parts in all the figures. There is an outer shell of iron or steel within which, at the bottom, is a flat hearth of floor 4 (Figs. 22, 23, and 25) of fire-brick, which supports a circular wall of like material, within which is the working chamber a of the furnace, and an outer wall, 6, concentric with the wall 5, extending upward a short distance and terminating substantially on a level with the bolster, forming lower ends of a pair of diametrically opposite embrasures, 7 and 8.

The wall 5 of the working chamber a is continued upward to the top of the outer shell 1, 2, 3; a feed chamber b for sulphur being formed between the walls 5 and 6 at bottom and between the wall 5 of the working chamber and the outer shell above the top of the outer wall 6.

The shell 1, 2, 3 terminates at top in a horizontal annular top portion, 9 (Figs. 22, 23, 24),
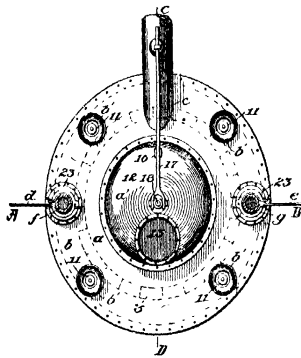
FIG. 24.

which is provided at suitable intervals with hoppers b' and with openings 10 (Fig. 23) at their bottoms, communicating with said feed space b, each of the hoppers being provided with a suitable plug 11, having a handle, 11', extending above the top of the hopper, so that the hoppers may be filled above the plugs, and the plugs then lifted to drop the contents of the hoppers into the feed space b, and quickly replaced to prevent the escape of fumes and the admission of air. Within the central opening of the top portion 9, of the shell, a charcoal hopper, a' (Figs. 22, 23, 24), is supported: this is constructed with a conical top, 12, provided with a capped charging neck,

13, through which the charcoal is introduced into the hopper, and a conical bottom, 14, depending within the upper end of the working chamber and provided with a central opening closed by a bell, 15; the top of the hopper being further provided with the supporting link 16 of a weighted lever, 17, connected with the said bell 15, by a rod, 18, and rendering the hopper a' normally closed at bottom. A discharge pipe, c (Figs. 23 and 24), extends from the working chamber a through the top portion 9 of the shell, in an oblique direction, as shown in Fig. 23.

Openings 19 and 20 (Figs. 22, 23, and 25) for the sulphur, are formed in the working chamber
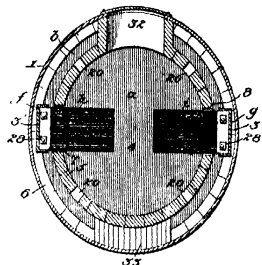
FIG. 25.

wall 5, immediately above the floor 4, and at one or more higher points, connecting the feed space b with the working chamber a, and pipe openings 21 and 22 extend through the outer wall 6 and the lower shell section 1 at different heights to allow the sulphur to enter the furnace proper. Metallic conductors, d and e (Figs. 22 and 24), connected with the source of electricity, are attached respectively to the protruding upper ends of metallic electrode stems f and g, which extend to the top of the outer wall 6, and rest upon the top of this wall, as in Fig. 22. Each of the electrode stems d and e is made in three sections, numbered respectively, 1', 2', and 3' in Fig. 22; the upper section 1' of each of the stems being hollow and cylindrical, and extending through a stuffing box, 23, mounted on the top of the shell, and preferably constructed with a water chamber, 24, for keeping the gland sufficiently cool. The lower end of the upper section has flanges 25, on opposite sides, adapting it to be coupled to the partly closed upper end of a flat middle section 2', which is tubular, excepting its lower end, and this end is trough-shaped in common with the lowermost section 3', which is detachably bolted to the trough-shaped lower end of the middle section 2'.

A pair of manholes, 26 and 27 (Fig. 22), in the middle section 2' of the outer shell, afford access to the bolts connecting the middle and lowermost sections 2' and 3' of the electrode stems, and facilitate disconnecting the lowermost sections 3' when the latter need to be renewed.

The electrodes proper, h and i, are of carbon, made in sections of different lengths, but all of one and the same size, and all rectangular in cross section (compare Figs. 22 and 25). Such carbon sections project at right angles from the

lower ends of the stems f and g, and may be clamped within the trough-shaped stem sections 3′. A sufficient number of the longer carbon sections are united at bottom to form the main body of each electrode and above these the shorter sections are arranged in steps, as shown in Fig. 22. The electrodes h and i project inwardly, as shown in Figs. 22 and 25, and are supported beneath by the bolster-forming lower ends of the embrasures 7 and 8, through which the respective electrodes extend toward each other, into the working chamber a, as shown in Fig. 22.

The tubular or hollow-stem sections 1′ and 2′ provide for feeding the material downwards upon the electrodes. The upper end of each stem is provided with a conical plug, 29, and with a gallows or yoke, 30, between which and the top of the plug 29 a wooden wedge, 31, is driven to render the closure air-tight.

In charging the furnace, the lower part of the working chamber a is filled with broken sulphur to the plane of the electrodes h, and a sufficient quantity of charcoal is superimposed. The lower part of the furnace is then tightly closed and sealed, and the working chamber a is thereafter filled with charcoal to any desired extent by way of the charcoal hopper $a′$ by depressing the bell 15 by means of the lever 17. The hopper $a′$ is then automatically closed at bottom by the re-elevation of the bell 15. Crushed sulphur is fed into the annular feed space b surrounding the working chamber wall from time to time as required by way of the hoppers $b′$, which are filled with the sulphur, and may serve to measure the quantity introduced, and are emptied into the feed space b by partly withdrawing their plugs 11 and replacing them immediately to prevent the entrance of air and the escape of fumes. The disulphide vapour, as it is formed, passes off through the pipe c into a suitable condenser

An upper manhole, 32, extending outward from the working chamber a through the shell sections 1 and 2, as shown in Figs. 22, 23, and 25, facilitates access to the interior of the furnace when it is cold for adjusting or renewing the electrodes h and i, and for arranging the charge at the beginning of an operation; and a subjacent manhole, 33 (Fig. 23), facilitates removing the ash from time to time as may be necessary. The electrode stems f and g, and their stuffing boxes 23,ʹ are insulated with mica and asbestos paper.

This furnace is designed to be 8 or 10 feet in diameter and 18 or 20 feet high, and will produce 5000 lbs. of carbon disulphide in 24 hours. Two electrodes only are employed.

Purification of Carbon Disulphide.—The crude product, which contains considerable quantities of sulphur, may be purified by distillation. The distilling vessel is made of sheet zinc, and is fitted in a water-bath. The vapours of carbon disulphide are passed through a wide tube into a worm surrounded by cold water, and ending in a lap at the bottom; the liquid as it condenses is allowed to trickle into a vessel placed to receive it.

Deiss employed large boilers with flat bottoms, which were 10 feet in length, 6½ feet in diameter, and 3¼ feet high. They had domed covers, externally coated by badly conducting material, so as to reduce to a minimum the amount of carbon disulphide returned to the boiler by condensation. The boiler was capable of receiving 5 tons of crude disulphide at a single charge, and had six delivery tubes which terminated in six vertically placed condensers. At the bottom of the boiler, there were two serpentine pipes, through one of which steam was passed until the crude carbon disulphide boils. For the purpose of distilling off the last portions steam was passed through the second serpentine pipe direct into the boiler, by which means carbon disulphide vapour and steam pass over together into the condensers, when the former accumulated in a layer below the surface of the water. The distillation of 5 tons lasted 3 or 4 days, and the products of the distillation at different stages were separately collected, and served for different purposes. In the first portions, foul-smelling constituents predominate, such as sulphuretted hydrogen; the intermediate portions are the purest, while the last portions are contaminated with sulphur. Much of the sulphuretted hydrogen was removed by placing a small quantity of caustic soda in the boiler.

Bonière purified the crude material by running it into a still containing a strong solution of caustic soda and heated externally by steam; the vapour was then passed through several other vessels of a similar kind containing alkaline liquids, solutions of salts of iron, lead, or copper, from which it was distilled and condensed. Millon patented a process which consisted in mixing the disulphide with half its weight of milk of lime, and then carefully distilling.

Sidot first distils the crude product, and then agitates it with mercury till the shining surface of the metal is no longer blackened by it. Carbon disulphide, when pure, is not affected by contact with mercury for any length of time. Or it may be shaken with 0·5 p.c. of mercuric chloride, which removes a fœtid compound of sulphur. The clear liquid is then decanted, 0·02 of its weight of an inodorous fat is added, and the mixture distilled in a water-bath at a low temperature (Cloez).

Another method of purification is to add to 100 parts of commercial product from 2 to 3 parts of dried copper sulphate, and to shake the mixture. The copper salt blackens and settles down, with removal of the smell of sulphuretted hydrogen. Absolute purity is obtained by again rectifying over dry copper sulphate. The latter can be rendered fit for further use by ignition, treating with sulphuric acid, and again igniting. The sulphide may be retained in a state of purity by allowing it to stand constantly over dry copper sulphate (J. Soc. Chem. Ind. 2, 246).

Singer has employed the following simple method with very satisfactory results :—

A cylindrical vessel, about 30 inches in diameter and 6 feet high, is provided with a perforated coil of lead pipe at the bottom. Into this vessel the impure carbon disulphide is run to about one-third its height. Lime-water is then pumped into it by means of a force-pump through the perforated coil. The lime-water, being specifically lighter than the carbon disulphide, rises to the surface, and, while traversing the body of the disulphide in a finely divided spray, the lime combines with the sulphuretted

hydrogen, &c. This washing is continued until the lime-water, which leaves this vessel through an overflow pipe near to the top, is perfectly clear. The carbon disulphide is now run into a still, about 1 p.c. its weight of a cheap colourless oil added, and covered with a layer of about 1 inch of water, to which some sugar of lead may be added. The carbon disulphide is now distilled in a water-bath and condensed in the usual way.

Carbon disulphide comes into the market in sheet-iron drums, the plates forming the top and bottom being bent inwards for their better protection from blows in moving about, and in the upper end there is an opening which can be closed by a screw stopper. Great care should be taken in the storing of carbon disulphide on account of its extreme volatility, the explosive nature of a mixture of the vapour with air, and the fact that its products of combustion are three irrespirable gases, viz. carbon dioxide, sulphurous oxide, and nitrogen. The store room ought to be isolated from other buildings, and should be well ventilated. The vessels in which the substance is kept ought to be tolerably large and placed where they are not likely to receive a blow or get thrown over. When required for use, the carbon disulphide can be drawn off by means of a siphon.

Properties.—Carbon disulphide is a colourless and extremely volatile liquid; the commercial product has a repugnant and fœtid smell, but when purified it has a sweetish ethereal odour, and an acrid pungent taste. It is highly refractive, its power in this respect being 1·645; its sp.gr. is 1·29215, 0°/4° (Thorpe). Water dissolves about $\frac{1}{1000}$ of its volume of the disulphide, and yields it up again unchanged on distilling; the solution in water possesses the odour of the disulphide, and has a slight burning taste. The aqueous solution acts as an antiseptic. Carbon disulphide dissolves sulphur, phosphorus, iodine, bromine, chlorine, camphor, caoutchouc, oils, and fats, and may be mixed in almost any proportions with alcohol, ether, benzene, and the fixed and volatile oils. Sulphur and phosphorus may be obtained in crystals by the spontaneous evaporation of their solutions in carbon disulphide. When a rapid stream of air is passed through it, the vapour, as it rises, is condensed to cauliflower-like masses, which make their appearance on the surface of the liquid (Wartha, Ber. 3, 80). When the whole of the liquid has disappeared, the resulting solid has a constant temperature of −12°, so long as it remains unvolatilised. According to Wroblewski and Olzewski, it solidifies at −116°, and remains solid for a considerable time, emitting a peculiar aromatic odour.

Carbon disulphide boils at 46·0° (Thorpe), 46·42° (corr.) (Thorpe and Rodger), and the vapour ignites in air at 149°. When mixed with three times its volume of oxygen, or an amount of air containing that volume of oxygen, it is very explosive. The flame of burning carbon disulphide is blue, and gives rise to sulphurous and carbonic acid gases: $CS_2 + 3O_2 = CO_2 + 2SO_2$. When carbon disulphide is burnt in a lamp on the principle of the Bunsen burner, and special precautions taken to prevent explosions, it produces a flame with an actinic power superior to that of magnesium (Compt. rend. 79, 1078).

A mixture of the vapour of carbon disulphide with nitric oxide burns with a blue flame, which is very rich in rays of high refrangibility, and on this account has been employed in photography.

Carbon disulphide is highly poisonous, inhalation of the vapour producing giddiness, vomiting, congestion, and finally coma. Even in small quantity only, it produces in time very serious effects on the nervous system. In the workmen employed in its manufacture, it causes weakness, depression, and loss of memory. Solution of ferrous carbonate in carbonic acid water has been found in some cases effectual as a remedy. Carbon disulphide vapour, when passed through a tube heated to bright redness, is partly resolved into its elements, carbon depositing and sulphur passing off with the undecomposed compound.

The following table represents its vapour tension at varying temperatures (Seyferth):—

45·5°	.	.	.	1 atmosphere
57·7	.	.	.	1½ „
66·9	.	.	.	2 atmospheres
74·3	.	.	.	2½ „
80·6	.	.	.	3 „
86·1	.	.	.	3½ „
90·9	.	.	.	4 „
95·5	.	.	.	4½ „
99·0	.	.	.	5 „

(For table of vapour pressures between 0° and 50°, v. Ramsay and Young, Chem. Soc. Trans. 47, 653; also Herwig, Pogg. Ann. 137, 69; 141, 83; 147, 161.)

The vapour of carbon disulphide, when passed over metallic oxides at a red heat, yields sulphur dioxide and carbon, together with metallic sulphides, which are generally found crystallised and resemble those found in nature. Carbon disulphide is one of the most powerful sulphurising agents known, and by means of it many sulphides may be produced which are not otherwise obtainable (Frémy). It converts oxides into sulphides when heated with them in sealed tubes. The vapour is strongly attacked by nitric acid, yielding sulphuric acid and nitrous vapours.

A mixture of the vapour of carbon disulphide and sulphuretted hydrogen, when passed over red-hot copper, yields copper sulphide and marsh gas: $CS_2 + 2SH_2 + 4Cu = 4CuS + CH_4$.

The vapour of carbon disulphide when passed over wood undergoing destructive distillation alters the character of the carbonaceous residue, producing a material having high conducting powers for heat and electricity, and extremely sonorous when struck.

Carbon disulphide is a powerful disinfectant. Meat and other putrescible bodies have been kept in an atmosphere containing its vapour for months without change.

Heated potassium burns in the vapour of carbon disulphide with formation of potassium sulphide and liberation of carbon.

When brought in contact with a solution of an alkaline hydroxide, carbon disulphide is decomposed, a carbonate and a sulphocarbonate being formed:

$$6KHO + 3CS_2 = 2K_2CS_3 + 3H_2O + K_2CO_3$$

When the vapour of carbon disulphide is

passed over heated calcium hydroxide, it is decomposed, carbon dioxide and sulphuretted hydrogen being evolved.

This reaction has been utilised in the removal of carbon disulphide from coal gas.

Chlorine has but little action on carbon disulphide at the ordinary temperatures, but in the presence of iodine, the chlorides of antimony and molybdenum, &c., chlorine replaces the sulphur with conversion of the carbon disulphide into carbon tetrachloride, and, if the action is interrupted before it is complete, intermediate compounds or sulphochlorides are formed (J. Soc. Chem. Ind. 6, 729).

Carbon disulphide combines with triethylphosphine $P(C_2H_5)_3$ to form a solid compound, crystallising in red crystals of the composition $P(C_2H_5)_3CS_2$.

Owing to its volatility it may be made to produce great cold by its own evaporation, and if this takes place very quickly under the air-pump, a temperature of $-60°$ may be obtained.

An aqueous or alcoholic solution of caustic potash, boiled with carbon disulphide, yields with lead salts a black precipitate of lead sulphide. This is a delicate test for the substance.

Carbon disulphide may be detected in coal gas by passing the gas when completely freed from sulphuretted hydrogen over red-hot copper foil, when the copper acquires an iridescent lustre, and its nitric acid solution diluted with water yields after some time a precipitate with barium chloride (A. Vogel, Zeitsch. anal. Chem [2] 6, 253).

Carbon disulphide combines with metallic sulphides, forming sulphocarbonates

$$CS_2 + Na_2S = Na_2CS_3$$
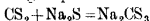
Sulphocarbonic acid is a yellow oily liquid, obtained by decomposing its potassium salt with hydrochloric acid

$$K_2CS_3 + 2HCl = H_2CS_3 + 2KCl$$
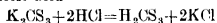
Potassium sulphocarbonate has been used for the destruction of phylloxera.

Uses.—Carbon disulphide is applied to a large number of useful purposes, the chief of which is in the preparation of vulcanised caoutchouc, and as a solvent for the latter in the manufacture of waterproof goods, by the deposition of a thin layer of the dissolved caoutchouc on the fabric; for the extraction of fat from crude wool; fatty oils from oil seeds and pressed residues; and for the purification of paraffin. It is used in the extraction of uncombined sulphur, and of bitumen from minerals. A solution of guttapercha in carbon disulphide is employed in making seamless joints and for the preparation of caoutchouc cement, various colours, ammonium thiocyanate, &c. It is also used for filling prisms on account of its high dispersive power.

Advantage is taken of its poisonous properties to expel weevils and other insects from stored grain without injuring the cereal. For this purpose, a small quantity of the carbon disulphide is sprinkled over the grain; both the larvæ and eggs are killed without injury to the grain (Doyère). It is also employed to destroy chicken lice and fleas, moths in furs, and in America to kill burrowing animals, such as gophers, ground squirrels, woodchucks, prairie dogs, rats, mice, moles, &c., and as a plant insecticide. It is used in Brazil to expel the Sauba ant from the foundations of houses. It may also be used in the analyses of oil seeds as a solvent for the purpose of ascertaining the proportion of oil which the ground seeds contain.

As carbon disulphide dissolves iodine in large quantity, but does not appreciably dissolve in water, it is employed for determining the amount of moisture in commercial iodine.

It may be used for dissolving quinine and other alkaloids; for extracting the aromatic principles from seeds and spices; and for the extraction of the scent of flowers. For these purposes, however, the purest quality of the disulphide can alone be employed.

A solution of phosphorus in carbon disulphide has been employed in the electrotyping of very delicate objects, such as grasses, flowers, feathers, &c. These are dipped into the solution, when, by exposure to the air, the carbon disulphide evaporates and leaves a thin film of phosphorus on the surfaces; they are then dipped into a solution of silver nitrate, by which silver is precipitated in a thin film, upon which, by the electrotype process, any thickness of silver, gold, copper, &c., can be deposited. If a few drops of carbon disulphide are put into a solution of silver cyanide, from which the metal is being electro-deposited, the silver is deposited bright, whereas without the disulphide it would be dull.

Deiss, who first employed carbon disulphide in the extraction of fatty oils from seeds, oil-cakes, and other pressed residues, used the following arrangement :—

Carbon disulphide was introduced into a large cemented brickwork reservoir, with a man-hole, which is generally kept closed, 22 feet long, 6 feet in diameter, and nearly 6 feet deep, and lined with lead up to the point to which it was filled with the disulphide and water, the latter being added as a thin layer to prevent the too rapid evaporation of the carbon disulphide. Immediately above this reservoir is a worm condenser, whose tail pipe dips into the liquid in the reservoir below ; on one side of the condenser there is an extractor having a capacity of 4400 gallons, and capable of receiving a charge of 12 tons of oilcake. This extractor is supplied by means of a pump with carbon disulphide from the reservoir below through a pipe leading up from the reservoir to the extractor. The latter apparatus has two perforated shelves, one nearly at the top and the other nearly at the bottom, between which the substance to be operated upon is placed. In the space between the lower perforated shelf and the bottom of the extractor is a coil of pipe through which steam can be passed. Just above the upper perforated shelf there are nine pipes on the same level for the purpose of carrying the vapours produced in the operation to the condenser. There are also pipes just above this shelf which are in direct communication with a still on the opposite side of the condenser, to which disulphide saturated with oil is carried, the saturated disulphide rising to the surface in the operation owing to the difference in the sp.gr. of the carbon disulphide (1·29) and oil (about 0·900). The still in which this liquid is distilled is about 11 feet long, 5 feet wide, and 15 inches deep, holding when half filled about 400 gallons. The liquid

is heated by steam supplied through two pipes coiled several times round the bottom of the still, and the vapour of the volatilised carbon disulphide is led through nine pipes into the condenser, and thence into the reservoir below the condenser, and is ready to be used again in the extractor for macerating a fresh quantity of material.

The time taken to fill the extractor with carbon disulphide is 8 hours, the maceration of the material 4 hours, the emptying of the contents of the extractor into the reservoir at the close of the operation 2 hours, and the steaming of the oil in the still in order to free it from carbon disulphide from 8 to 12 hours Working with an apparatus such as described, about 2½ tons of oil can be obtained in 30 hours from 25 tons of oilcake.

Extraction of fat from wool --Morson and Jerome employ for this purpose a large cylindrical vessel with a close-fitting cover and double walls, between which hot water circulates The wool is placed on a perforated shelf near the bottom of the cylinder, whilst a perforated plate, a kind of piston, could be pressed upon the wool by an arrangement of screws Carbon disulphide is pumped from a reservoir into the extractor, and as the liquid becomes saturated with fat it is led through a pipe into a still, heated by a coil of steam pipe at the bottom, the vapour being passed to a worm condenser and the liquid disulphide passed into the reservoir which is immediately beneath. By a second arrangement of steam pipes, steam can be passed directly into the still so as to remove the last portions of disulphide. A current of air, heated to 70°, is then forced through the wool by means of an air-pump. As all the parts of the apparatus are in direct communication with each other, it is necessary to supply the diminished pressure in the reservoir. When air is pumped out of it and sent through a tube several times bent and the last portion fitted with a hot-water jacket, the equilibrium of pressure should be maintained, and this is done by a supply of air from a gas-holder in connection with the apparatus The last portions of carbon disulphide are thus swept out of the extractor and are carried through a pipe into a second worm condenser, and thence to the reservoir. At convenient points between the macerating vessel and the still, as well as at the ends of the condensing worms, there are windows in the pipes, which serve to form an idea of the state of the operation, and close to each of these windows is a cock from which a little of the liquid can be drawn and evaporated, in order to see if a residue of fat remains.

The macerating vessel or extractor is charged with about 10 tons of wool, which is then reduced to about half its bulk by screwing down the perforated plate. The carbon disulphide is pumped into the extractor, and, after filtering through the wool, ascends through the perforations and passes into a pipe leading to the condenser. This is continued until the liquid comes over colourless, and leaves no residue on evaporation. When the extracting process is finished, the cock admitting carbon disulphide into the extractor is closed, and a partial vacuum is formed by drawing air out of the extractor by the air-pump, the greater part of the disulphide adhering to the wool being carried with it at

the first few strokes. The water-jacket is then heated by water at 70°, and the cocks are so arranged as to allow the heated air to pass through the wool, and thence into the open air. By this method a considerable quantity of fatty substance is obtained from sheep's wool which was formerly lost.

The following materials are treated with carbon disulphide in order to obtain fatty matters from them :—

1. The dark-coloured residues of stearin manufactories, which are products of the treatment with sulphuric acid. They yield from 18 to 20 p.c. of fatty acid, which was formerly almost entirely lost. The residues are mixed with sawdust to facilitate the filtration of the dissolved portion.

2. The dark-brown cart-grease from the axles of carts, carriages, &c. This is first treated with sulphuric acid, washed, and dried.

3. Tow and rags used in cleaning machinery. This treatment of rags, &c., has a threefold advantage ; recovery of fat or fatty acids, purification of the rags so that they can be used again, and the prevention of spontaneous combustion, which these materials are liable to on exposure to air.

4. The refuse of the preparation of beeswax, which on treatment with carbon disulphide yields a yellow wax useful for many purposes.

5. Sawdust that has been used for filtering oils after purification with sulphuric acid.

6. The sediment produced by the treatment of various oils with sulphuric acid contains about 50 p.c. of oil, which may be extracted by carbon disulphide after washing with boiling water, drying, and mixing it with sawdust.

7. Bones from slaughter-houses and kitchens to be used in the preparation of bone-black yield to carbon disulphide from 10 to 12 p.c. of fat.

8. The expressed residues of oil seeds, such as rape, sesamé, flax, &c., when they cannot be properly employed as fodder. In all cases it is necessary to break up the oilcake into small pieces before treating it with carbon disulphide, so as to ensure thorough penetration of this substance. The residue left after extracting the fat is hardly suitable for fodder, but is valuable as a manure.

9. The 'cracklings' or greaves obtained by the melting of tallow.

10. The pressed cacao beans from which no further cacao butter can be obtained by pressing.

11. The pressed residues obtained in the preparation of olive oil.

Extraction of bitumen, &c., from minerals.— Carbon disulphide can be employed in the extraction of bitumen from mineral bodies which contain so small a percentage as not to pay when obtained by the ordinary process of distillation. The apparatus used consists of a close reservoir for the carbon disulphide, over which is a cooling apparatus which serves as condenser. Below the reservoir are two filters provided near the bottom with perforated shelves. Minerals are introduced into the filters upon the shelf through doors near the bottom, which are then closed and made air-tight. Carbon disulphide is now admitted through a pipe at the bottom of each filter, and as the liquid rises it percolates through the minerals, dissolving out the bitumen,

and when full flows out at the top through a pipe leading to a still, where the saturated liquid is distilled, the vapour of carbon disulphide ascending into the condenser, and the liquid carbon disulphide as it condenses trickles into the reservoir beneath. The bituminous matters, which remain in the still, are drawn off by a cock at the bottom, and the disulphide which remains absorbed by the minerals in the filters is expelled by a current of steam. This apparatus is practically continuous, very little loss of the disulphide taking place at each operation, and as much as 12 p.c. of bitumen can be obtained, whereas only 7 or 8 p.c. could be had by distillation.

Extraction of spices, &c.—Bomère has devised an apparatus for extracting the aromatic principles of various spices and other substances used for seasoning food, by means of carbon disulphide. It is on the same principle as the apparatus already described, and consists of a series of wire-gauze sieves arranged one over the other in an air-tight case. The carbon disulphide is made to pass through the sieves, which contain the substance to be operated upon, *e.g.* pepper, thus dissolving out the active principles, and as it reaches the top it flows through a pipe into a boiler. The boiler contains salt, sugar, lactose, dextrin, saltpetre, or other material. The liquid is distilled in the boiler, by admitting steam into a kind of jacket, when the disulphide distils over and is condensed in a worm condenser, while the salt or sugar remains behind, retaining all the aromatic or active principles of the spice.

Bergot has constructed an apparatus for rapidly determining the quantity of oil in seeds, &c., by means of carbon disulphide It consists of a glass vessel in the neck of which a cylindrical glass vessel is accurately fitted, and at the side in a tubulure is inserted a small air-pump. 50 grams of the finely ground seed to be examined are placed in the cylindrical glass vessel, and are covered with a diaphragm upon which 50 more grams are placed and covered with a second diaphragm. Carbon disulphide is now poured on until the seed is fully moistened, and after a few minutes a partial vacuum is made in the apparatus by means of the air-pump, when the pressure of the air drives out the disulphide and oil in solution into the vessel beneath. This is repeated until the carbon disulphide comes off colourless and leaves no oily stain on contact with filter paper. About 400 or 500 grams of carbon disulphide are sufficient to exhaust the above amount of seed.

The oily solution thus obtained is heated over a water-bath, and as soon as the disulphide is expelled, the residue is allowed to cool and is weighed.

H. L. Greville has extracted with advantage the carbon disulphide absorbed in the purifiers of the gasworks. The lime used for this purpose, after being discharged from the purifiers, is introduced into a boiler capable of receiving a charge of several hundredweights, fitted with a perforated false bottom, pressure gauge, and an arrangement for admitting steam. The yield of carbon disulphide from 100 tons of spent lime is about 1½ tons. In addition to the value of the crude product thus obtained, the lime

remaining is, with a small addition of fresh lime, fit for further use in the purification of coal gas. As is well known, oxide of iron, after continued use in the absorption of sulphuretted hydrogen from coal gas, contains about 50 p.c. of free sulphur. The crude carbon disulphide, obtained as described, can be used for the extraction of this sulphur, and the oxide which remains is revivified, and is again fit for purifying purposes. The sulphur is recovered by distillation, and the carbon disulphide can be used over again (J. Soc. Chem. Ind. 2, 488).

The principal seats of manufacture of carbon disulphide in England are London, Manchester, certain towns in Yorkshire, and Ironbridge ; in France, Paris, Bordeaux, and Marseilles. Germany, Austria, and Sicily have several manufactories.

Carbon monosulphide (xCS). A reddish-brown powder obtained by exposing carbon disulphide to sunlight. Insoluble in water, alcohol, turpentine, and benzene (Sidot, Compt. rend. 69, 1303 ; 74, 180 ; 81, 32).

It is also formed when thiocarbonyl chloride reacts at ordinary temperature with nickel carbonyl: xCSCl$_2$+xNi(CO)$_4$=xNiCl$_2$+$4x$CO+(CS)$_x$. The reaction also takes place at $-20°$, although more slowly. The nickel chloride produced is extracted with water, and the brown residue is dried by heating at $100°$, then at $150°-200°$ under reduced pressure.

Carbon monosulphide has sp.gr. 1·6, but after compression into a solid block the sp.gr. is 1·83. It is a non-conductor of electricity. In concentrated sulphuric acid it forms a purplish-brown solution, the colour of which is destroyed on boiling, when carbon dioxide and sulphur dioxide are evolved. When poured into water the purplish-brown solution yields the unchanged monosulphide. It also forms brown solutions in aqueous or alcoholic ammonia, in ammonium sulphide, in potassium-hydroxide sulphide and hydrosulphide. With nitric acid it gives a red solution. When heated in a vacuum at 360° or below, no change takes place, only a small quantity of hydrogen sulphide is evolved, but at a dull red heat it decomposes thus :

$$2(CS)_x = xC + xCS_2$$
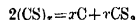
When carbon disulphide vapour at low pressure is subjected to the action of the silent electric discharge, sulphur is deposited, and probably gaseous carbon monosulphide is evolved. The gas can be collected in a tube cooled with liquid air, when it condenses together with carbon disulphide. If the temperature of the condensing tube is allowed to rise, the monosulphide polymerises with explosive violence to the brown solid carbon monosulphide (CS)$_x$. In presence of excess of carbon disulphide, the gaseous monosulphide is fairly stable under certain conditions even at high temperatures, but it is completely decomposed when passed through 10 c.m. of a red-hot tube packed with asbestos. (Dewar and Jones, Proc. Roy. Soc. 1910, 83, A, 408, 526. *See* also Dunn, Chem. Soc. Proc. 1910, 116 ; Dewar and Jones, *ibid.* Trans. 1910, 1226 ; Dewar and Jones, Proc. Roy. Soc. 1911, 85, 574.)

Carbon oxysulphide or **Carboxyl sulphide** or **Carbonyl sulphide** COS. Discovered by Than, in 1867 ; occurs in certain hepatic waters or

mineral springs. Prepared (1) by passing a mixture of carbonic oxide and vapour of sulphur through a hot tube : $CO + S = COS$.—(2) By the action of sulphuric acid upon potassium or ammonium thiocyanate :

$$CNKS + 2SO_4H_2 + OH_2$$
$$= COS + SO_4HK + SO_4(NH_4)$$
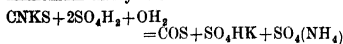
The gas is purified by passing it successively through strong caustic alkali, concentrated sulphuric acid, and finally through a mixture of triethylphosphine (1 part), pyridone (9 parts), and nitrobenzene (10 parts). It is then cooled to $10°-20°$, and the last traces of impurities are removed by liquefying it, when the impurities remain uncondensed (Hempel, Zeitsch. angew. Chem. 1901, 14, 865).—(3) By heating together sulphur trioxide and carbon disulphide : $CS_2 + 3SO_3 = COS + 4SO_2$ (Armstrong).—(4) By heating urea with carbon disulphide in a sealed tube to $110°$: $COH_4N_2 + CS_2 = COS + CNS·NH_4$. The oxysulphide is given off together with hydrogen sulphide on opening the tube, and the latter is absorbed by passing through lead acetate (Ladenburg). It is also formed in the combustion of carbon disulphide with oxygen (Dixon and Russol, Chem. Soc. Trans. 1899, 619), and by the passage of the dark electric discharge through a mixture of carbon disulphide and carbon monoxide (Losanitsch and Jovitschitsch, Ber. 1897, 30, 135).

Properties.—It is a colourless gas, and odourless when quite pure (Stock and Kuss). It acts strongly on the nervous system, a rapid overpowering action following the inhalation of small quantities. It is readily inflammable, and forms with oxygen an explosive mixture (Russell, Chem. Soc. Trans. 1900, 356). The gas is soluble in water, 1 c.c. dissolving 0·8 c.c. of the gas at 13·5° and 756 mm. pressure. The solution gradually decomposes, forming hydrogen sulphide and carbon dioxide. A platinum wire heated to whiteness in the gas decomposes it into sulphur and carbonic oxide, the latter occupying the original volume of the gas. It has a specific gravity of 2·1046, and may be easily poured from one vessel to another. When burnt in air, it produces carbon dioxide and sulphur dioxide. With caustic alkalis, it yields a mixture of carbonate and sulphide

$$COS + 4KHO = CO_3K_2 + K_2S + 2H_2O$$
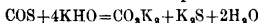
Carbon oxysulphide reacts with solutions of metallic salts, forming the metallic sulphide and carbon dioxide, and is readily oxidised to carbon dioxide and sulphuric acid by bromine water or acid permanganate.

It is slowly decomposed by acid cuprous chloride, thus :

$$COS + 2CuCl + H_2O = CO_2 + 2HCl + Cu_2S$$
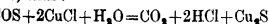
(Berthelot, Ann. Chim. Phys. 1898, [7] 14, 205).

With magnesium organic compounds, it can be employed in the synthesis of thio-acids and of *s*-trisubstituted carbinols (Wiegert, Ber. 1903, 36, 1007).

Its critical temperature is 105°, and its critical pressure is 60 atmospheres. It is liquefied at a pressure of 12·5 atmospheres and temperature 0° to a colourless, mobile, and highly refractive liquid, D—87° 1·24; m.p —138·2°, boiling at −50·2°, at 760 mm., which dissolves sulphur and mixes with alcohol and ether, but not with water (Ilosvay, Bull. Soc. chim. [2] 37, 294 ; Stock and Kuss, Ber 1917, 50, 159).

CARBON SUBOXIDE (*Carbon carbonyl* ; *Carbonyl ketene* ; *Malonic anhydride*) C_3O_2. Discovered in 1906 by Diels and Wolf. Prepared by distilling ethyl malonate under reduced pressure into a vessel containing a large excess of phosphorus pentoxide and some glass wool, the vessel being kept at a temperature of 300°. The resulting products are passed through a dry tube, and then into a vessel immersed in liquid air to condense the ethylene and carbon suboxide. The ethylene volatilises from the mixture at the ordinary temperature, leaving a small quantity of colourless liquid. This is volatilised and collected in a tube kept at between 60° and 70° (Diels and Wolf, Ber. 1906, 689). Diels and Meyerheim (*ibid.* 1907, 355) showed that carbon suboxide may be obtained by similar methods from methyl, benzyl, and phenyl malonates and also from ethyl methanetricarboxylate ; and that by heating malonic acid at $140°-150°$ there is formed acetic acid, carbon dioxide, and about 10–12 p.c. of carbon suboxide. Staüdinger and Bereza obtained carbon suboxide by treating malonyl chloride with silver, lead, or zinc oxides ; the yield is only 10 p.c. (Ber. 1908, 1461). By treating an ethereal solution of dibrommalonyl chloride with zinc shavings, a method similar to that for preparing the ketenes, Staüdinger and Klever obtained a 50–80 p.c. yield of carbon suboxide (Ber. 1908, 906). Stock and Stoltzenberg (Ber. 1917, 50, 498) find that the poor yields of carbon suboxide usually obtained by the action of phosphoric oxide on malonic acid are largely due to the polymerisation of the suboxide under the catalytic influence of the dehydrating agent, and they describe an apparatus in which the suboxide is rapidly removed by carrying out the reaction in a vacuum and condensing the product by liquid air.

The pure oxide is a colourless, very mobile, refractive liquid with a pungent smell resembling acetaldehyde and mustard oil. It is poisonous. It boils at 7° under 761 mm., and its vapour density corresponds to the formula C_3O_2 ; m.p. −107° (−111·3° Stock and Stoltzenberg) ; density of liquid 1·11. On passing the vapour through a constricted tube, a metallic mirror resembling arsenic is obtained. At low temperatures, carbon suboxide is quite stable, but between 0° and 15° a trace of impurity rapidly polymerises it to a red solid. This polymeride is very hygroscopic, and on addition of water, heat is developed, carbon dioxide evolved, and an eosin-red solution formed : by heating the red compound carbon dioxide, carbon monoxide and carbon suboxide are formed, and at higher temperatures, carbon monoxide and dioxide are produced, the residue being a mixture containing more carbon than is required for carbon suboxide. By keeping carbon suboxide for 2 days in a sealed tube at 15°, it completely changes into the polymeride, forming a dark-red solid mass, soluble in water to a dark-red solution ; this change is instantaneous at 100°. Carbon suboxide burns with a bright-blue but smoky flame, forming carbon dioxide. Carbon suboxide does not combine with aldehydes, Schiff's bases or hydrogen cyanide (Diels and Lalin,

Ber. 1908, 3426), but in liquid sulphur dioxide at $-40°$ to $-50°$ forms a white crystalline compound with formic acid, and a colourless syrup with acetic acid; the constitution of these compounds is doubtful. Water quickly reconverts it into malonic acid.

Two formulæ have been proposed for carbon suboxide; Diels and Wolf represent it as the anhydride of malonic acid $O : C : C : C : O$; Michael (Ber. 1906, 1915; 1908, 425), as the lactone of β-hydroxypropiolic acid $C\underset{C}{\overset{CO}{<}}O$.

The first formula seems to be correct, for the following reasons (v. Diels and Blumberg, Ber 1908, 82, 1233) :—

(1) B p. 7°. Propiolic acid boils at 144°, and if β-hydroxypropiolic acid had a boiling-point, it would boil higher still, and its lactone would certainly not boil at so low a temperature as 7°.

(2) The values for the molecular refraction and molecular dispersion are high : $M_D = 16·6$; $\gamma - a = 0·736, 0·739, 0·862$ (three determinations).

(3) Similarity of carbon suboxide to the metallic carbonyls.

(4) Similarity to the isocyanates and ketenes.

(5) Addition of four atoms of bromine to form dibrommalonyl bromide and the regeneration of carbon suboxide from this compound

(6) The following chemical reactions :—

$O:C:C·C·O + 2H_2O = HOOC·CH_2·COOH$ (malonic acid)
$O:C:C:C:O + 2HCl = ClOC·CH_2·COCl$ (malonylchloride)
$O.C:C.C:O + 2NH_3$
  $= H_2N·OC·CH_2·CONH_2$ (malonamide).
$O:C.C:C:O + 2C_6H_5·NH_2$
  $= C_6H_5·HN·OC·CH_2·CONH·C_6H_5$ (malonanilide).
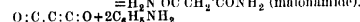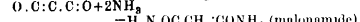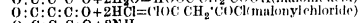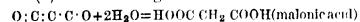
(7) The improbability of the existence of a β-lactone containing two carbon atoms triply linked together (v. KETONES).

CARBONADO v. DIAMOND.

CARBONITE, or natural coke. A coke-like material formed by the baking action of intrusive igneous rock-masses on seams of bituminous coal. Found in Ayrshire and in Chesterfield co., Virginia.   L. J. S.

CARBONITE. An explosive consisting of nitroglycerine, 25–27 parts; barium nitrate and potassium nitrate, 30–36 parts; wood meal, 40–43 parts; sodium carbonate, 0·5 parts (v. EXPLOSIVES).

CARBONYLS. Metallic compounds of carbon monoxide. The existence of this class of compounds was first made known in 1890, when Mond, Langer, and Quincke discovered that carbon monoxide, passed over heated, finely divided nickel, yielded a colourless volatile liquid.

Iron, cobalt, molybdenum, and ruthenium have since been found to yield carbonyls by similar treatment.

The production of the carbonyl is facilitated by conducting the operation under pressure and, in most cases, at a fairly high temperature.

For the production of the iron and nickel compounds, the carbon monoxide is simply passed over the heated metal, but for the other compounds a special apparatus is used. This consists of a nickel-steel tube, in the form of a test-tube, capable of withstanding a pressure of 500 atmospheres and a temperature of 450°. It is copper lined to prevent the action of carbon monoxide upon the iron. The carbon monoxide under pressure is led in through a pressure valve

and down a copper tube reaching almost to the bottom of the nickel-steel tube, where it comes in contact with the metal to be experimented upon, contained in a glass tube loosely fitted to the top of the apparatus. The excess of the carbon monoxide, and other vapours, escape through a pressure valve and pass through a tube immersed in a freezing mixture, in which any compound that is formed is collected (Chem. Soc. Trans. 1910, 97, 798).

The carbonyls have very similar chemical properties. Upon heating, in some cases an intermediate compound is formed, but they all decompose ultimately, yielding the metal, which is deposited as a bright mirror, and carbon monoxide. Dilute acids are practically without action upon them, but strong acids decompose them readily, giving the corresponding salt, with the evolution of carbon monoxide and hydrogen The halogens also decompose them. All are decomposed by moist air, giving precipitates of the metallic hydroxides and, in some cases, what is probably a hydrated basic carbonate. They are more or less soluble in the common organic solvents, but all are insoluble in water.

In physical properties, they vary considerably ; thus, in volatility, they range from the non-volatile $Fe_2(CO)_4$ of sp.gr. 2·08 to the very volatile $Ni(CO)_4$ of sp.gr. 1·32. They are highly coloured, except in the cases of molybdenum and nickel carbonyls, which are white and colourless respectively. Some can exist in the three states of solid, liquid, and vapour, and others in only one or two of these phases.

Owing to their diversity in composition, a general chemical formula cannot be assigned to them, but it is probable that they are similarly constituted. A ring formula, e.g. $Ni\overset{CO\cdot CO}{\underset{CO\cdot CO}{<}}$ does not explain all their properties, and the compound $Fe_2(CO)_9$ cannot be brought into line with the other compounds which only contain one atom of the metal. Presumably they have a molecular rather than an atomic constitution (Mond, Hertz and Cowap, l.c.). The various known carbonyls are described under the several metals.

CARBORUNDUM (*Crystalline silicon carbide*) SiC. This compound was discovered accidentally by Acheson, in 1891, and is now manufactured under his patent (Eng. Pat. 17911, 1892) by the Carborundum Co. at Niagara Falls, U.S.A., and to a smaller extent in Canada.

Preparation.—Amorphous silicon carbide is formed by heating carbon and silica together at about 1200°, as a greenish powder (Schutzenberger, Compt. rend. 114, 1089), but carborundum is only formed at a temperature of 1950° (Tucker and Lampen, J. Amer. Chem. Soc. 1906, 28, 853) (1820° according to Gillett), which is attained by means of the electric arc. Moissan thus prepared pure silicon carbide from the vapours of carbon and silicon (Compt. rend. 1893, 114, 1089).

The method of manufacture used at Niagara is as follows :—The furnaces are built of firebrick and are about 16 feet long × 5 feet high × 5 feet wide. The ends are solid, about 2 feet thick, and carry the terminals. Each terminal consists of 60 carbon rods, 30 inches long and

3 inches diameter, into the ends of which fit copper plugs which in turn fit into sockets in a square copper plate bolted to the outside of the wall, and connected with the leads. Only the °end walls and the bed are permanent; the sides are built up with the charge and taken down to remove the product.

In charging, the furnace is half filled with the materials, which must not touch the electrodes; and a cylindrical core 2½ inches diameter, composed of pieces of coke ¼-¾ inch diameter, is built up between the electrodes. Over this the charge is built up to a height of 8 feet. The current passes through the coke and forms numerous arcs which heat the charge to a very high temperature. The charge is composed of:

Coke	.	.	.	.	34·2 parts
Sand	.	.	.	.	54·2 ,,
Sawdust	.	.	.	9·9 ,,
Salt	.	.	.	.	1·7 ,,

The salt is added as a flux; the sawdust to increase the porosity of the charge and allow the escape of the carbon monoxide formed in the reaction:

$$SiO_2 + 2C = Si + 2CO$$
$$Si + C = SiC$$
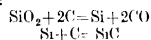
During the run, about 6 tons of this gas are given off; it is allowed to burn at the top of the furnace.

The alternating current supplied by the Niagara Power Co. at 2200 volts is transformed down to 165 volts, and a large water rheostat is used to regulate or interrupt the current, the usual means being too dangerous with the heavy currents used. At the beginning of a run, the E.M.F. is 165 volts, but within 1½ hours the resistance decreases and the E.M.F. is reduced to 125 volts; during this period, the current increases from 1700 amperes to 6000 amperes. The conditions then remain steady during the whole run of 36 hours.

A modification of the process consists in preheating the charge by combustion of gaseous or solid fuel (Tone and the Carborundum Co. U.S. Pat. 908357, 1908). By moving the position of the arc relatively to the charge, the process may be made continuous (ibid. U.S. Pat. 937119, 1909).

The charge per furnace is about 30,000 lbs., of which the core forms about 3 p.c., the energy used is about 26,400 kilowatt-hours, and the product contains about 6700 lbs. of carborundum and 5000 lbs. of amorphous silicon carbide.

The carborundum is dug out in large masses and pounded with water in a mechanical crusher, and then digested with sulphuric acid (1 : 2) for 3 days at 100°, and finally washed with water. The finer portions, which are washed away, are collected separately and known as *flours*. The residue is dried in a kiln and graded through a system of screens. *Hand-washed powders* are of various grades of fineness, according to the length of time they remain suspended in water (Kohn, J. Soc. Chem. Ind. 1897, 863).

Some analyses of these products are tabulated above :—

	I.	II.	III.	IV.	V.
Si	70·00	69·93	62·70	69·10	65·42
C	30·00	29·90	32·26	30·20	27·93
Al₂O₃ } Fe₂O₃ }	—	—	0·93	0·46	5·09
CaO	—	—	—	0·15	0·38
MgO	—	—	0·11	—	0·21

I. is the calculated composition for SiC; II. is Moissan's pure product (Compt. rend. 1893, 114, 1089); III. is commercial carborundum; IV. is the same after purification by Mühlhäuser's method—heating in oxygen for 1 hour and treating with hot sulphuric and hydrofluoric acids (Dingl. poly. J. 1893, 289, 164); V. is amorphous silicon carbide.

Weber has patented a method of production from kaolin and coke in the electric furnace. The product is treated with water, which decomposes the aluminium carbide, leaving the carborundum (U.S. Pat. 728528, 1903).

The production of a dense, compact variety, by the action of the vapours of carbon and silicon upon silicon carbide has been patented by the Carborundum Co. (U.S. Pat. 913324) and by Bouvier (Fr. Pat. 350369, 1904). It is very hard, resists acid, and is a good insulator.

Its preparation from silicon monoxide and carbon has been described by Potter and Westinghouse (U.S. Pat. 875673, 1907).

Carborundum may be formed in pure carbon and afterwards converted into carborundum by heating to a very high temperature in a bed of finely powdered carborundum or of sand and carbon (Bolling, Eng. Pat. 6693, 1905; D. R. P. 195533; Fr. Pat. 353017).

Properties.—Carborundum crystallises in flattened hexagonal rhombohedra, having an adamantine lustre and a hardness of 9·5 (Mühlhäuser, Zeitsch. anal. Chem. 1893, 637). The colour of the commercial product is greenish-grey to yellow or blue; obtained pure from pure materials, the compound is colourless. Its sp.gr. is 3·23 at 15° (Fitzgerald, J. Soc. Chem. Ind. 1897, 246).

It is infusible and quite unaffected up to a temperature of 2220°, when it decomposes into silicon and graphitic carbon (Tucker and Lampen, J. Amer. Chem. Soc. 1906, ·28, 853). Acids have no action upon it, but it is attacked by fused alkalis with formation of a silicate and carbon.

The determination of silicon in carborundum is made by converting it to silicate as above, and precipitating as silica; carbon is estimated by oxidising the finely powdered substance with lead chromate (Matthews, J. Soc. Chem. Ind. 1895, 755; Mühlhäuser, Zeitsch. anal. Chem. 1893, 637).

Uses.—Carborundum is used chiefly instead of emery as an abrasive. Though it is more costly, it does the same work more effectively in one-third to one-fourth the time (Mühlhäuser, l.c.). The powder is used in glass cutting and grinding, and for polishing.

It is made up into wheels, hones, &c., by mixing with moistened kaolin and felspar, moulding under hydraulic pressure, and firing

the articles in a kiln for 7 days. Other binding materials, such as shellac, are used for special purposes, and papers, similar to emery paper, are made. The binding material may be dispensed with by moulding the carborundum with water and then heating the articles to 2500°F. in an oxidising flame (Imray, Eng. Pat. 9963, 1904 ; Tone, U.S. Pat. 772262).

Carborundum can be used instead of diamond for drill heads, if incorporated in a suitable metallic or ceramic matrix (Bouvier, Fr. Pat. 375338, 1907).

Silicon carbide is used instead of ferro-silicon as a source of silicon in steel making. About 0·1–0·4 p.c. is placed in the ladle and dissolves readily in the molten steel, ensuring solid castings (Kaufmann and Bouvier, Fr. Pat. 344906, 1904 ; Eng. Min. J. 75, 481).

The amorphous silicon carbide, formerly a waste product, is used for making highly refractory firebricks and the retorts for zinc distilling (Chesneau, Ann. Chim. anal. appl. 1908, 13, 85). A refractory cement is made from carborundum 90–60 parts, fireclay 10–40 parts, lime 0–4 parts, and water-glass solution 47°Bé. 20–50 parts, mixed, dried, and repowdered (Müller, Fr. Pat. 338914, 1903).

Neumann has shown that silicon carbide reduces silver, copper, nickel, and lead from the chlorides (Chem. Zeit. 1900, 24, 1013).

By the action of silicon carbide on metallic oxides, many metallic silicides may be obtained. This reaction may be used for the preparation of special ternary or quaternary steels at a single operation (Baradac-Muller, Soc. Mg. Cie. de France, Proc.-verb. 1908, 245).

o-**CARBOXYPHENYLTHIO-G L Y C O L L I C ACID.** o - **CARBOXYPHENYLTHIOLACETIC ACID** v. PHENYLTHIOGLYCOL-o-CARBOXYLIC ACID.

CARBURINE, Trade name for a variety of petroleum spirit ; sp.gr. 0·68. Used as an ' enricher ' of coal gas.

CARCLAZITE or **CARCLAZYTE.** A name suggested by J. H. Collins (The Hensbarrow Granite District, Truro, 1878) for the china-clay-rock from which china-clay is prepared. So named from the Carclaze mine, near St. Austell, in Cornwall. L. J. S.

CARDAMOM OIL v. OILS, ESSENTIAL.

CARDAMOM SEEDS. *Cardamomi Semina,* B.P. The dried ripe seeds of *Elettaria Cardamomum* (Maton).

CARDINAL-RED, Syn. *Acid magenta* (v. TRIPHENYLMETHANE COLOURING MATTERS).

CARDOL. A non-volatile oil found in the pericarp of the cashew nut, *Anacardium occidentale* (Linn.).

CARICIN. An oil found in the seeds of the papaw tree, *Carica papaya* (Linn.) (Peckolt, Pharm. J. [3] 10, 343).

CARMINAPH v. AZO- COLOURING MATTERS

CARMINAPH GARNET v. AZO- COLOURING MATTERS.

CARMINAZARIN v. COCHINEAL.

CARMINE. The red colouring matter extracted from the cochineal insect. It is of somewhat variable composition, containing besides the colouring matter some organic matter from the insects and a little of the salt used to precipitate it from solution.

Preparation.—The powdered cochineal is boiled with water, the solution filtered or allowed to settle, and the colouring matter precipitated by addition of some salt, such as alum, stannous chloride, cream of tartar, Roman alum, &c. The precipitate is allowed to settle, and collected. Sometimes fish glue or white of egg is added before precipitation. Carmine is somewhat soluble in water and very freely soluble in alkaline solutions. The whole of the colouring matter is immediately precipitated by alum in the form of a lake.

In dyeing with carmine, a mordant of alum or stannous chloride is used. Kielmeyer recommends the following mixture for printing on woollen goods : 14 kilos. gum, 17·5 kilos. cochineal lake, and 2·25 kilos. fustic lake, are mixed and warmed with 15 lit. water till the gum is dissolved, then 1 kilo. of oxalic acid and 1·75 kilos. acid sodium oxalate added, and the mixture allowed to cool, after which 2·25 kilos. sodium acetate are added. After printing, the fabric must be dried for a day or two, steamed under a slight pressure, and washed in a stream of water.

Detection of carmine in cloth.—Alcohol takes no colour from the cloth, but when it is boiled in solution of aluminium sulphate the solution turns red and the colour is unchanged by the addition of acid sodium sulphate.

The absorption spectrum of carmine in alkaline solution is remarkable, showing two dark bands between the lines D and E very similar to those of blood. Murexide and madder show no such bands. When wine is coloured with carmine, the characteristic absorption bands cannot be seen unless more than 12 p.c. of the total colour is due to carmine (Gautier), but the adulteration can be detected by adding alum, when the colour changes to a rose tint.

It is said that the finest shades of carmine can only be obtained by working in direct sunlight (v. COCHINEAL).

CARMINIC ACID v. COCHINEAL.

CARMOISINE. Syn. for *Azorubin* (v. AZO-COLOURING MATTERS).

CARMUFELLIC ACID $C_{12}H_{20}O_{16}$. An acid crystallising in thin plates, said to be formed by the action of nitric acid on oil of cloves (Muspratt and Dawson, Phil. Mag. [4] 2, 293).

CARNALLITE. Hydrated double chloride of potassium (KCl 26·8 p.c.) and magnesium, $KCl \cdot MgCl_2 \cdot 6H_2O$. It occurs abundantly in the uppermost layers (' carnallite zone ') of the beds of abraum-salts in the Prussian salt déposits, and is the chief commercial source of potassium chloride. It is also found at Wittelsheim in Upper Alsace. The mother-liquor, remaining after the potassium chloride has crystallised out, contains traces of bromine and rubidium, the former of which is a valuable by-product. Thallium has also been detected in traces. When pure, the mineral is colourless and water-clear, but it is often coloured yellowish or reddish by intermixed impurities. Red carnallite owes its colour and metallic sheen (resembling that of sunstone) to the presence of minute scales of hæmatite. Crystals are rare ; they are orthorhombic, and have the form of six-sided pyramids with numerous well-developed faces. Owing to the extreme deliquescence of the salt, crystals must be preserved in sealed vessels.

Carnallite and bromocarnallite, in which bromine takes the place of chlorine in the above formula, have been prepared artificially from solutions containing a large excess of magnesium chloride and at a temperature of over 25°.　L. J. S.
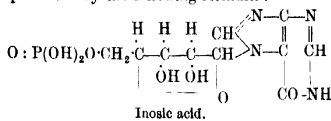
CARNAÜBA WAX or **CARNAHUBA WAX** v. WAXES.

CARNAÜBIC ACID $C_{23}H_{47}COOH$ is obtained from Carnaüba wax ; m.p. 72·5° (Stürcke, Annalen, 1884, 223, 283 ; Darmstaedter and Lifschütz, Ber. 1896, 619, 2899).
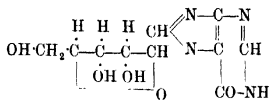
CARNELIAN v. CHALCEDONY.

CARNINE is the name given to a base isolated from meat extract by Voit (Weidel, Annalen, 1871, 158, 353) ; it occurs also in beer yeast extract (Schutzenberger, Chem. Zentr. 1877, 73), in the muscle of some fresh-water fish and frog's flesh (Kruckenberg and Wagner, ibid. 1884, 107), and in beet juice (v. Lippmann, Ber. 1896, 29, 2645). Carnine crystallises in chalk-white druses, is sparingly soluble in cold, readily so in hot, water, insoluble in alcohol or ether ; it forms a crystalline hydrochloride and platinichloride, and a sparingly soluble compound with silver nitrate (Weidel, l.c.).

Haiser and Wentzel (Monatsh. 1908, 29, 157) have shown that carnine is an approximately equal molecular mixture of hypoxanthine and inosine $C_{10}H_{12}O_5N_4$, and the two are separated by the action of acetic anhydride which converts the inosine into the acetate $C_{10}H_9O_2N_4(OAc)_3$, m.p. 236° (decomp.). Inosine crystallises in silky needles, m.p. 215° (decomp.), $[\alpha]_D^{18°}$ -49·2°, and 100 c.c. of aqueous solution saturated at 20° contains 1·615 grams. When inosine is hydrolysed by sulphuric acid it yields hypoxanthine and a pentose, originally termed carnose by Levene and Jacobs (Ber. 1909, 42, 2102, 2474). and afterwards identified with a-ribose. Inosine is closely related to inosic acid (hypoxanthine phosphoriboside) (Levene and Jacobs, ibid. 1910, 43, 3147 ; Proc. Amer. Soc. Biol. Chem. 1910, 25 ; Haiser and Wentzel, Monatsh. 1909, 30, 147), for by heating a dilute aqueous solution of barium inosate at 125°–130° for 6 hours, inosine and barium phosphate are formed. The relation between the two compounds is probably represented by the following formulæ :

$$O : P(OH)_2O \cdot CH_2 \cdot \overset{H}{\underset{}{C}} - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - \overset{CH}{\underset{}{C}} \overset{N—C—N}{\underset{N—C}{\diagdown}} \overset{}{\underset{O}{CH}} \overset{}{\underset{CO-NH}{}}$$

Inosic acid.

$$OH \cdot CH_2 \cdot \overset{H}{\underset{}{C}} - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - \overset{CH}{\underset{}{C}} \overset{N—C—N}{\underset{N—C}{\diagdown}} \overset{}{\underset{O}{CH}} \overset{}{\underset{CO-NH}{}}$$

Inosine.
M. A. W.

CARNITINE $C_7H_{15}O_3N$, a base isolated from Liebig's beef extract and present also in fresh beef ; is readily soluble in water yielding an alkaline solution ; the nitrate crystallises in needles and has $[\alpha]_D$ about $-22°$; the platinchloride $C_{14}H_{32}O_6N_2$,PtCl$_6$ forms minute orange-red needles, m.p. 214°–218° (decomp.) (Gulewitsch and Krimberg, Zeitsch. physiol. Chem. 1905, 45, 326) ; the hydrochloride is hygroscopic and lævo-rotatory. The aurichloride

$$C_7H_{16}O_3NAuCl_4$$
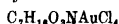
forms pale yellow needles and orange needles or prisms, m.p. 150° ; the mercurichloride

$$C_7H_{15}O_3N,HCl,6HgCl_2$$
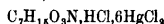
is an oil that slowly crystallises ; the compound $C_7H_{15}O_3N,2HgCl_2$ has m.p. 196°–197° (Krimberg, ibid. 1907, 50, 361). The monoacetyl derivative of the hydrochloride $OAc \cdot C_7H_{14}O_2N$,HCl forms a yellow crystalline platinichloride

$$(C_9H_{16}O_3N)_2PtCl_6$$

m.p. 199° (Engeland, Ber. 1909, 42, 2457). The ethyl ester is identical with Kutscher's oblitine (Zeitsch. Nahr. Genussm. 1905, 10, 534), (Krimberg, Zeitsch. physiol. Chem. 1908, 58, 417 ; Ber. 1909, 42, 3878 ; Engeland, l.c.).

Carnitine is identical with Kutscher's novaine (Krimberg, Zeitsch. physiol. Chem. 1908, 55, 466 ; Engeland, Ber. 1909, 42, 2457), and is probably a hydroxy derivative of a betaine, since on reduction with hydrogen iodide and red phosphorus at 130°, it yields a product identical with Willstatter's γ-trimethylbutyrobetaine

$$NMe_3 \diagdown \overset{CH_2 \cdot CH_2}{\underset{O —— OC}{}} \diagup CH_2$$
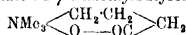
(Ber. 1910, 35, 584 ; see also Fischer and Goddertz, Ber. 1910, 43, 3272–3280). Krimberg (Zeitsch. physiol. Chem. 1907, 53, 514). According to Engeland (Ber. 1909, 42, 2457 ; 43, 2705) and Rollett (Zeitsch. physiol. Chem. 1910, 69, 60), carnitine hydrochloride is the chloride of a-hydroxy-γ-trimethylamino-n-butyric acid

$$NMe_3Cl \cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot CO_2H ;$$
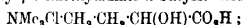
the isomeride, β-hydroxy-trimethylamino butyric acid chloride crystallises in needles, gives a chloroaurate, m.p. 145°, which decomposes 225° (Engeland, ibid. 1910, 43, 2705–2707). V. BETAINES.
M. A. W.

CARNOSINE $C_9H_{14}O_3N_4$, a base isolated from Liebig's extract of beef (see Smorodinzew, Zeitsch. physiol. Chem. 1913, 87, 20 ; ibid. 92, 19 and 227, for the percentage of carnosine found in muscle extracts) is soluble in water, crystallises in rosettes of large colourless needles, m.p. 246°–250° (decomp.). It has $[\alpha]_D+21$ independently of the concentration (Gulewitsch (Zeitsch. physiol. Chem. 1913, 87, 6–11), and has a strongly alkaline reaction. The vapours of carnosine give the pyrrole reaction with a pine splinter, Gulewitsch (ibid. 87, 8) Carnosine may be precipitated from an aqueous extract of muscle by a saturated solution of mercuric sulphate in 5 p.c. sulphuric acid ; the precipitation is accelerated by the addition of two volumes of alcohol and a little ether (Dietrich, Zeitsch. physiol. Chem. 1914, 92, 212–213). Smorodinzew (ibid. 214–220) recommends a 10 p.c. solution of mercuric sulphate in 5 p.c. sulphuric acid solution. Carnosine can be isolated by precipitation with a copper salt, Mauthner (Monatsh. 34, 883–900). The nitrate $C_9H_{15}O_3N_5$ crystallises in large stellate clusters of needles, m.p. 219° (decomp.), $[\alpha]_D^{19·5°}+22·2$, $p=7·603$ p.c., $c=7·820$ p.c. The rotatory power increases slightly on dilution ; it falls to about

half its value in presence of nitric acid (Gule-witsch, *ibid.* 1–6); the *copper* derivative

$$C_9H_{14}O_4N_4Cu$$

is crystalline and decomposes at 220°. The *silver* derivative and acyd double salt with silver nitrate closely resemble the corresponding derivatives of arginine (Gulewitsch and Amiradžibi, Ber. 1900, 33, 1902). Carnosine is probably identical with Kutscher's *ignotine* (Zeitsch. Nahr. Genussm 1905, 10, 528; Gulewitsch, Zeitsch. physiol. Chem. 1906, 50, 204; 51, 258; 52, 527). Compare, however, Kutscher (*ibid.* 1907, 50, 445; 51, 545).

When carnosine is hydrolysed by boiling with barium hydroxide it yields histidine, the other product of hydrolysis being probably alanine

$$C_9H_{14}O_3N_4 + H_2O = C_6H_9O_2N_3 + C_3H_7O_2N$$
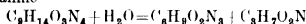
According to Gulewitsch (Zeitsch physiol. Chem. 1911, 73, 434–446) three-quarters of the carnosine nitrogen belongs to histidine and the rest to β-alanine.

That carnosine is β-alanylhistidine is shown by its synthesis from histidine and β iodopropionyl chloride (Baumann and Ingvaldsen, J. Biol. Chem. 1918, 35, 263). This is further proved by its behaviour towards 2 4 5-trinitrotoluene. It has been synthesised by condensing β-nitropropionyl chloride with histidine methyl ester and reducing the resulting products with stannous chloride and hydrochloric acid (Barger and Tutin, Bio-Chem. J. 1918, 12, 402).

The carnosine content of flesh extracts may be estimated by two colorimetric methods which control one another; the one depends on the colour yielded by the histidine complex in the carnosine molecule with diazobenzene-sulphonic acid (Weiss and Sobolev, Biochem Zeitsch. 1913, 58, 119–129); the other on the violet colour yielded by carnosine when boiled with cupric hydroxide, Furth and Hryntschak (Biochem. Zeitsch. 1914, 64, 172–194).

M. A. W.

CARNOTITE, A hydrated vanadate of uranium and potassium, occurring abundantly as a bright canary-yellow powder disseminated in sandstone in western Colorado. C. Friedel and E. Cumenge (Compt. rend. 1899, 128, 532), by whom it was first described and named (after A. Carnot), expressed the composition by the formula $2U_2O_3 \cdot V_2O_5 \cdot K_2O \cdot 3H_2O$. Detailed analyses were made by W. F. Hillebrand (Amer J. Sci. 1900, 10, 120), and he concluded that the mineral is not simple, but a mixture. This view is, however, not borne out by T. Crook and G. S. Blake (Min. Mag. 1910, 15, 271), who find that the material, both from Colorado and from South Australia, is definitely crystallised in minute plates possessing orthorhombic symmetry and with characters analogous to those of autunite $[Ca(UO_2)_2P_2O_8,8H_2O]$. The original material was found by M. and Mme Curie to contain radium and polonium.

The carnotite-bearing sandstones occur over an extensive tract of country on both sides of the Colorado-Utah boundary, the richest deposits being in the neighbourhood of La Sal Creek, Roc Creek, and Paradox Valley, in Montrose Co., and in San Miguel and Dolores Cos., in southwest Colorado; other deposits are met with near Coal Creek in Rio Blanco Co. and Skull Creek in

Routt Co. in north-west Colorado, and at Mauch Chunk, Pennsylvania. Most of these deposits are in Jurassic (La Plata) sandstone, but some of those in the N.W. are in sandstones of Cretaceous age. They have been mined at several spots, and a plant for the extraction of uranium, radium, and vanadium salts has been erected near Cedar in San Miguel Co., Colorado; but the sandstone ore is of a low grade, and the difficulties of transport are considerable. An average sample of marketed ore assayed U_2O_3 11·49 p.c. and V_2O_5 6 40 p.c. (R. B. Moore and K. L. Kithil, U.S. Bureau of Mines, Bull. 70, 1913; C. L. Parsons and others, *ibid.* Bull. 104, 1915).

In South Australia, at Radium Hill, near Olary, carnotite occurs in films on the joint-planes of a large deposit of ilmenite rutile, and magnetite.

A closely allied mineral, named *ferganite* (I. A. Antipov, 1908; Abstr. in Jahrb. Min. 1909, ii, 38), is a hydrated vanadate of uranium and lithium. It occurs, together with other uranium minerals, in prov. Fergana in Russian Turkestan.

L. J. S.

CARO'S ACID. Monopersulphuric acid (*v.* SULPHUR).

CAROBS. Specimens of commercial carobs are found to possess the following percentage composition : water, 9–13 ; nitrogenous compounds, 5–7 ; cellulose, 8–12 ; fat, less than 1 ; ash, 2 ; sugars (dextrose and sucrose in variable proportions), 30–43 ; phosphoric oxide, 0·16–0·21 (Balland, J Pharm. Chim. 1904, [6] 19, 569).

CARONE *v.* KETONES.

CARONY BARK *v.* CUSPARIA BARK.

CAROTIN. The colouring matter of *Daucus carota* (Linn.). Found also in the leaves of plants to the extent of 0·1 to 0·2 p.c. (Arnaud, Compt. rend. 1890, 109, 911) in full vegetation, and to a slight extent in etiolated leaves (Immendorf, Chem. Zentr. 1890, i. 163), and in the tomato ; is present in maize, squash, orange-peel, flax seed, mustard seed, black sesamé seed, palm oil, but not in rape seed, white sunflower seed, turnip, safflower, cotton seed or turmeric. It forms the colouring matter of yellow and orange pollen ; the oily drops on the surface of the pollen of *Verbascum thapsiforma* contain not less than 6·6 p.c. of carotin ; and in the animal kingdom it occurs as the colouring matter of milk-fat, hence in butter and the body-fat. *corpus luteum* and skin secretions of the cow ; it constitutes the yellow lipochrome of blood-serum and is found in *Diaptomus bacillifer* (Blanchard, Compt. rend. 1890, 110, 292). It can also be extracted from stinging-nettle leaves with light petroleum (Willstätter and Mieg, Annalen, 1907, 355, 1). Carotin crystallises in copper-coloured leaflets which appear red by transmitted light, and have m.p. 167·8°. It is insoluble in water, readily soluble in carbon disulphide or benzene, sparingly so in alcohol, ether, petroleum, or chloroform. Carotin is able to decompose carbon dioxide with formation of oxygen, and this probably explains why etiolated leaves can, under certain conditions, generate oxygen (Kohl, Chem. Zentr. 1906, ii. 442).
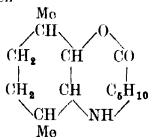
Carotin is an unsaturated hydrocarbon having the formula $C_{40}H_{56}$ (Willstätter and Mieg. *l.c.*) ; it combines with iodine to form the *iodide* $C_{40}H_{56}I_4$, which crystallises in rosettes

of dark-violet prisms, and decomposes at 140°-170°; and the *iodide* $C_{40}H_{56}I_3$, which forms dark-violet plates and decomposes at 136°-137°. The *bromo-* compound $C_{40}H_{56}Br_{23}$ decomposes at 171°-174° (Willstätter and Escher, Zeitsch. physiol. Chem. 1910, 63, 47). Carotin dissolves slowly in concentrated sulphuric acid, forming an indigo-blue solution from which the hydrocarbon is precipitated in green flakes on the addition of water; it absorbs oxygen to the extent of 34·3 p.c. of its weight, yielding a colourless substance. When carotin is oxidised with a small amount of acetic acid solution of chromic anhydride, and the temperature kept below 30°-40°, an *oil* $C_{40}H_{56}O_8$, or $C_{40}H_{50}O_4$, is obtained, and this does not solidify at −104° (Euler and Nordenson, Zeitsch. physiol. Chem. 1908, 56, 223).

Carotin has no appreciable toxic acid; quantities of 0·2 gram injected into guinea-pigs had no effect on the health of the animals.

CAROUBIN and **CAROUBINOSE.** According to Effront (Compt. rend. 1897, 125, 38), the seeds of *Ceratonia siliqua*, used as a cattle food in Portugal, contain a carbohydrate, *caroubin*, which, when purified, forms a white spongy friable mass, giving with water a thick syrup or jelly. By hydrolysis, it yields *Caroubinose* ($C_6H_{12}O_6$), which has about the same reducing power as dextrose. Is probably identical with mannose (Van Ekenstein, Compt. rend. 125, 197) (*v.* CARBOHYDRATES).

CARPAINE $C_{14}H_{25}O_2N$ occurs in papaw leaves (*Carica Papaya* (Linn.)). It forms glancing prisms, m p. 121°, $[\alpha]_D + 21°\,55'$, and has a bitter taste (Greshoff, 1890, Med. s'Lands Plantentuin, Java, No. 7, 5; van Rijn, Arch. Pharm. 1893, 231, 184; 1897, 235, 332). According to Barger (Chem. Soc. Trans. 1910, 97, 466) it is a lactone of carpamic acid $C_{14}H_{27}O_3N$, and may be written

Me

$$\begin{array}{c} \diagup CH \diagdown \quad O \diagdown \\ CH_2 \quad CH \quad CO \\ \mid \qquad \mid \qquad \mid \\ CH_2 \quad CH \quad C_5H_{10} \\ \diagdown CH \diagup \diagdown NH \diagup \\ Me \end{array}$$

CARRAGEEN. *Carageen, Carragheen,* or *Carraqaheen.* (Fr. *Gaëmen.*) *Irish or Pearl moss.* An alga (*Chondrus crispus*) found on all the western coasts of Europe and on the east coast of North America. In Ireland it is collected, dried, and bleached in the sun. Found in commerce as flat, dry, yellow-white pieces 2 to 3 inches long, usually branching, of a very faint odour and mucilaginous taste, swelling in water like gelatine. Almost completely soluble in boiling water; the solution sets to a jelly on cooling. Contains a high percentage of nitrogen, and is of value as a food in diseases of lungs and general weakness, usually taken dissolved in hot milk. It has also been applied as a size and for stiffening silk, also occasionally in making jellies.

Sometimes found largely adulterated with *Gigartina mamillosa*, which is less valuable and recognised by its stalked fruits and channelled stem (*v.* ALGÆ AND IRISH MOSS GUM, ART GUMS.

CARRAWAY OIL *v.* OILS, ESSENTIAL.

CARRIAGE VARNISH *v.* VARNISH.

CARROT, the tap root of *Daucus carota* (Linn.). Several varieties exist, and the roots are employed as cattle food and as a table vegetable. Kellner gives as the average composition :

Water	Protein	Fat	Sol. carbo-hydrates	Fibre	Ash
87·0	1·2	0·2	9·3	1·3	1·0

According to American analyses, the average composition of the edible portion, as a table vegetable, is :

Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
88·2	1·1	0·4	9·2		1·1

The Belgian white carrot is often used for the field crop, whilst the red carrot is preferred for table purposes. The reddish colouring matter of the carrot, carotin, is sometimes used in colouring butter and cheese. It has the composition $C_{40}H_{56}$, and can be obtained by rasping the roots, precipitating the juice with lead acetate, with which the carotin forms a lake. This is dried and extracted with carbon disulphide. The solution is evaporated to dryness and repeatedly extracted with cold petroleum spirit in order to remove the phytosterols. The residue is then dissolved in carbon disulphide, from which the carotin is precipitated by the addition of alcohol It can then be recrystallised from benzene in the form of rhombic plates with a metallic lustre, blue by reflected, orange-red by transmitted light. The substance which Husemann discovered in the carrot and called hydrocarotin is a mixture of sitosterol and stigmasterol, and consists of the same phytosterols as are found in other plants (Beschke, Ber. 1914, 47, 1853) (*v.* CAROTIN).

As a farm crop, carrots are particularly valued for horses and dairy stock. They are best grown on light land, free from stones and weeds and well tilled. H. I.

CARROT GUM *v.* GUMS.

CARVACROL *v.* CAMPHORS ; also OILS, ESSENTIAL

CARVEOL *v.* CAMPHORS.

CARVOL *v.* CAMPHORS ; also OILS, ESSENTIAL.

CARVONE *v.* KETONES.

CASCARA SAGRADA, B.P. ; U.S.P. The dried bark of the *Rhamnus Purshiana* (DC.), a small species of thorn tree inhabiting the Pacific slopes of the Rocky Mountains. (For botanical characters, *see* Hooker (Flora Bor. Amer. 43), Prescott (Amer. J. Pharm. 1879, 165), Möller (Pharm. J. [3] 14, 467), Moss (*ibid.* [3] 649, 19).) Cascara sagrada had been long known as a cathartic to the Indians and trappers of California, when it was later introduced into American and European medicine. Its physiological action is similar to the other and better-known *Rhamnus frangula* (Linn.), but the *Purshiana* is the more esteemed. (*Cf.* Kennedy, Amer. J. Pharm. 1885, 498.)

Cascara bark has been examined by Prescott (*ibid.* 1879, 165) ; Limousin (J. Pharm. Chim. [5] 6, 80) ; Wenzell (Pharm. Rundsch. 1886, 79) ; Meier and Webber (Pharm. J. [3] 18, 804) ; Schwabe (Arch. Pharm. 226, 569) ; Zeig (Pharm. J. [3] 20, 173) ; Le Prince (Compt. rend. 115, 286), Dohme and Engelhardt (Amer. Chem. J. 20, 534) ; but the statements made regarding it

are very conflicting, for a summary of which *see* Jowett (Rep. Amer. Pharm. Assoc. 1904, 1), who has also made an exhaustive examination of the bark. He has confirmed the presence of *emodin* together with a small proportion of an isomeric substance which may be identical with the *iso-emodin* obtained from *Rhamnus frangula* by Thorpe and Miller (Chem. Soc. Trans. 61, 6). Glucose is also present, and a substance which, on treatment with acid, yields syringic acid. No evidence was obtained of the existence of chrysophanic acid or chrysarobin or of glucoside yielding on hydrolysis emodin, chrysophanic acid, or rhamnetin. The cascarine of Le Prince and the purshianin of Dohme and Engelhardt are probably impure products. Emodin is not the active principle of the drug, and no clue could be obtained as to the nature of this principle. (Compare Nouveaux Remèdes, 1909, 471, where the active principle is stated to be precipitated by lead acetate and ammonia, after treatment with lead acetate alone.) It is a light yellow powder of bitter taste, probably a glucoside. According to Tschirch and Monikowski (Arch. Pharm. 1912, 250, 92) the patent cascara-preparation 'peristaltin' consists of a mixture of glucosides, hydrolysed by steam to rhamnose, chrysophanic acid, emodin methyl-ether and *cascarol* $C_{18}H_{10}O_5$, yellow needles, m.p. 218°. Cascara bark contains about 2 p.c. of fat and a small proportion of a volatile oil The constituents of *R. Californica* appear to differ very little from those of *R. Purshiana.* For methods for the estimation of the active constituents of Cascara sagrada, *see* Warin (J. Pharm. chim. [6] 22, 12), whose colorimetric method is approved by Tschirch and Pool (Arch. Pharm. 1908, 246, 315). For differential tests of Cascara and *Rhamnus frangula*, *see* Kroeber (Schweiz. Woch. Chem. Pharm. 1910, 48, 377); Beal and Okey (J. Amer. Chem. Soc. 1917, 39, 716). For standards for the evaluation of liquid extracts of Casacara and *Rh. frangula,* *see* Apot. Zeit. 1913, 39, 579).   G. B.

CASCARILLA BARK, *Cascarilla* (B.P.). The bark of *Croton Eluteria* (Benn), or ' seaside balsam,' a euphorbiaceous tree growing in the West Indies.

Duval obtained from it a substance, *cascarilline* $C_{12}H_{18}O_4$, m.p. 205°, which Alessandri (Arch. Pharm. 220, 690) also isolated by extracting the bark with oxalic acid and precipitating the extract with ammonia. This substance dissolves in hydrochloric acid, producing a rose-coloured solution, which changes through purplish-red, violet, and green to a sky-blue without the addition of water. The drug also contains betaine (Naylor, Pharm. J. 59, 279), and 1·5 p.c. of an essential oil (*q.v.*).   G. B.

CASCARILLA OIL *v.* OILS, ESSENTIAL.

CASEIN. Casein occurs in the milk of mammals, and is the principal protein of cow's milk, which, up to the present, is its only commercial source. Cow's milk contains, on an average, about 3 p.c. of casein, which exists in a suspended or colloidal condition, probably as a lime compound in combination with calcium phosphate, giving the milk its opaque appearance. This can easily be proved by allowing the milk to pass through a filter of unglazed porcelain, when a white mass of casein and fat will be found on the surface of the filter, and the

filtrate will contain the lactose, soluble albumen, and soluble salts of milk.

Preparation of pure casein. Separated milk is diluted to about five times its volume with water and sufficient acetic acid added to give 0·1 p.c. of acid in the solution. The casein is precipitated, carrying down with it the fat. The curd is washed about ten times by decantation, collected on a cloth filter, washed, and pressed as dry as possible. It is then dissolved in the least quantity of ammonia, and filtered. The filtrate is precipitated with acetic acid, washed, and redissolved in ammonia. This process is repeated three or four times. The curd is then rubbed up in a mortar several times with 80 p.c. alcohol, and finally with absolute alcohol. It is next similarly treated with ether, and extracted with ether in a Soxhlet apparatus, and the casein finally dried at 100°C.

Properties —Thus prepared, casein is a white, amorphous body without taste or smell. It is very sparingly soluble in water, and quite insoluble in alcohol and ether. Its most probable percentage composition is : C, 53·13 ; H, 7·06 : N, 15·78 ; P, 0·86 ; O, 22·40 ; S, 0·77.

Casein is a phospho-protein. Its molecular weight is stated to be about 1135. It is a weak dibasic acid, forming acid and neutral salts with alkalis. In dilute alkaline solutions, it has a lævo-rotatory action on polarised light. At the ordinary temperature, 1 gram of casein combines with 9 c.c. of N/10 hydrates or carbonates of alkalis, and with nearly 7 c.c. decinormal solutions of common acids. It is soluble in caustic alkalis, and in the carbonates, bicarbonates, phosphates, &c., of the alkali metals, and is precipitated unchanged by addition of sufficient acid to neutralise the alkali.

Casein is soluble in strong hydrochloric acid, giving a fine violet colour, and is also soluble in dilute hydrochloric acid containing 0·2 p.c. of the fuming acid, but is insoluble in 2 or 3 p.c. acid.

Preparation of industrial casein. There are many methods of preparing casein, but on the large scale these are generally limited to three :

(1) Precipitation by means of acid—usually sulphuric, though acetic, phosphoric, lactic, hydrochloric, &c., are also employed.

(2) Curdling by means of rennet.

(3) Curdling by ' self-souring.'

A very interesting method of preparation is by means of electricity, but so far this does not seem to have progressed beyond the laboratory stage. The method, however, will be described later. Whichever method be employed, the first essential is a machine-separated milk, containing the smallest possible quantity of fat. Milk taken from cows shortly after calving, and containing colostrum, is unsuited for casein manufacture. It gives a soft curd which squeezes through the filter cloths, and holds a great deal of water. It has sometimes been found necessary to throw away a whole batch as the curd has been quite unworkable.

Also, if the milk has been pasteurised at such a high temperature that some of the lact-albumin becomes insoluble, the curd will give a great deal of trouble.

The milk from the separators is run into a tank of suitable dimensions, and brought to the required temperature by means of steam.

Precipitation by sulphuric acid.—The requisite quantity of sulphuric acid, previously diluted with water in a wooden or enamelled iron bucket, is then introduced, and the whole well agitated, when the milk will gradually lose its opaque appearance and become clear with separation of the curd. As soon as the whey is yellow and transparent, the agitation is stopped, and the curd falls to the bottom of the tank. The whey is run off, the curd allowed to drain and washed with cold water until all the whey has been separated. The bulk of the water is then removed by means of a suitable press or by a centrifugal machine.

Curdling with rennet.—The amount of rennet required depends upon the acidity of the milk and the temperature. The more acid the milk and the nearer the temperature approaches 106°F., the less is the rennet required. At 118·5°F. and at 86°F., the curdling power of rennet is only about 70 p.c. of that at 106°F.

If the acidity of the milk be 15°, about 2½ oz. rennet should curdle 100 gallons of milk in about ¼ hour.[1] When the acidity reaches 30°, half this quantity will suffice. The requisite quantity of rennet is diluted with water and thoroughly stirred into the milk at a temperature of about 106°F. The milk is then allowed to rest until it has 'set' like a junket. The mass is cut up into small cubes by special knives, and then agitated gently at first, and afterwards vigorously while being very slowly heated up to about 120°F. by means of free steam or a steam-jacket. The curd will then be in hard grains or nodules at the bottom of the tank. The whey is rapidly run off, the curd washed well with cold water, and pressed.

Curdling by 'self-souring.'—When milk is exposed to the air, it becomes acid. This change is effected by the *Bacillus acidi lactici*, which converts the lactose into lactic acid. When sufficient acid has been formed, the curd separates from the whey. On the large scale, the separated milk is run into a tank, the temperature brought to and maintained at about 98°F., at which point the growth of the bacilli is most rapid. After some hours, according to the freshness of the milk, a sour smell will be noticed and the milk will begin to curdle. When the right point has been reached, steam is turned on and the mass agitated in order to make the curd firm, and in a suitable condition for washing and pressing. The whey is then run off and the curd finished in the usual manner.

Drying of the curd.—When as much moisture as possible has been removed from the curd, it is broken up and dried. This may be effected either by spreading on trays in heated drying-rooms fitted with ventilating appliances to facilitate the removal of the moisture, or in a drying cylinder heated from inside or outside or both, and rotated to keep the contents in constant motion. Another method of drying the curd is by means of a Passburg vacuum drier, consisting of a cast or wrought-iron case, which can be hermetically closed by doors. A vacuum is produced by an air pump, and the moisture is vapourised at a low temperature so that drying is soon effected.

[1] The 'degree of acidity' of milk is the number of c.c. of $N/10$-NaOH sol. required to neutralise the acid in 100 c.c.

Whatever process be adopted, the temperature must be carefully watched, as a few degrees too much heat will 'burn' the casein to a rich brown colour, and if the temperature be too low the curd will take a long time to dry, and may become sour and mouldy.

The dry casein is then ground to a fine powder, when it is ready for the market.

Curdling by electricity.—Although this process is so far not a commercial one, it is sufficiently interesting to warrant a short description. The milk is heated to 120°F., and a porous cell, containing dilute milk, is placed in the centre. A current of electricity of sufficient tension is passed, and the soluble elements, the phosphates in particular, are decomposed. The anode is placed in the milk and the cathode in the porous cell. Phosphoric acid is then liberated in the milk, and causes the precipitation of the casein, while the liquid in the porous cell becomes strongly alkaline. The chief difficulty lies in the choice of electrodes—the cathode in the porous cell can be carbon, but the anode must be of platinum, which makes the original cost very heavy. Any of the common metals are attacked in a very short time, and carbon throws off small particles which cause the precipitated curd to become black. It is, of course, possible to have both electrodes of carbon in porous cells, but it is found that the curd soon fills up the pores and the action becomes very slow.

Properties.—Industrial casein, prepared with sulphuric acid, will dissolve in the following quantities of alkalis or alkaline salts, though larger quantities are always used in the various industries :—

	Per cent.
Sodium bicarbonate	3½
Sodium carbonate	2¾
Sodium hydroxide	1¾
Sodium silicate 140°Tw.	10
Sodium arsenate	20
Sodium sulphite	9
Strontium hydrate	20
Trisodium phosphate	8
Ammonia, ·880	2½
Sodium tungstate	12½
Borax	9½

Solutions of the hydroxides of potassium, sodium, lithium, and ammonium of equal concentration, dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly ; strontium hydroxide dissolves it most rapidly, calcium hydroxide more slowly, and barium hydroxide more slowly still.

Rennet casein is insoluble in carbonate and bicarbonate of soda, partly soluble in borax and ammonia, and soluble in trisodium phosphate and lime.

Its solution in alkalis does not coagulate on heating, but is precipitated by acids and many metallic salts. When acted on by formaldehyde and certain other bodies, casein is rendered insoluble. Advantage is taken of this fact in various industries to give a waterproof coating of casein.

Pure casein contains only a very small amount of ash, but industrial casein may contain up to about 7 p.c. or 8 p.c.—rennet-prepared

casein containing the most, and 'self-soured' casein the least.

For the analysis of commercial casein v. Hopfner and Burmeister, Chem. Zeit. 1912, 36, 1053 ; Analyst, 1912, 493.

Uses of casein. Casein is employed in a large number of industries, and its use is increasing every year, in fact, there are but few industries in which casein, in some shape or form, is not or cannot be employed with advantage.

The greater quantity of imported casein comes from the Argentine. Large quantities also are received from France and Germany, and smaller quantities from Holland, Belgium, and the United States.

Casein is used in paste and dry distempers ; in cardboard manufacture, paper glazing, leather dressing, soap manufacture, cotton sizing, dressing for textiles, finishing, waterproofing, calico printing, cask glazing , imitation bone, ivory, tortoiseshell, amber, ebony, &c. ; picture mouldings, sealing for bottles, cabinet and pianoforte making, emulsions, fining wines, boot polishes, waterproof cements, polishes, films, diabetic and protein foods.

Alimentary casein. Some of the best-known food preparations of casein are :

Plasmon.—This is a cream-coloured powder, somewhat coarse in texture. It is a soda compound of casein, and is partially soluble in water. It contains nearly 2 p.c. of lactose (milk-sugar) and about 70 p.c. of proteins.

Sanagen.—A fine white powder, completely soluble in water. It is a compound of casein with about 5 p.c. of sodium glycerophosphate made by a special process. It contains about 76–78 p.c. proteins, and is practically free from lactose, and so is specially recommended for diabetic patients.

Sanalogen.—A white powder soluble in water. It consists of casein with about 5 p.c. of sodium glycerophosphate, and is free from fat and lactose.

Dr. Reigel's milk protein.—A soda compound of casein, soluble in water. According to the patent specification, the curd is precipitated from the milk by means of ethyl-sulphuric acid.

Eucasein.—A casein-ammonia compound, soluble in water.

Nutrose.—A soda compound of casein.

Casein solids. *Galalith.*—Insoluble casein, treated with formaldehyde and subjected to heavy pressure, gives plates of great hardness, and by blending pigments with the casein, imitations of bone, ivory, ebonite, &c., are obtained. The products are known as *Galalith* (from the Greek *gala*, milk, and *lithos*, stone). It is prepared from a specially pure casein, precipitated by rennet, from sweet milk freed from fat by centrifuging. The curd is drained and dried, forming lumps 8–12 mm. thick. These are ground to a pasty meal, which is moistened with water, coloured as required, worked up by steel helices to a plastic mass, which is then hot-pressed in hydraulic presses. The pressed cake is hardened in a solution of formaldehyde, the length of treatment varying from 2 to 30 weeks, according to the thickness of the articles, whereby the casein acquires the qualities of horn (Bonwitt. Zeitsch. angew. Chem. 1914, 27, 2). The following articles are

made from galalith : brush-backs, combs, cigar and cigarette holders, penholders, electrical fittings, umbrella and stick handles, buttons, dominoes, &c. Being uninflammable, casein possesses great advantages over celluloid. It is a bad conductor of electricity, and is therefore suitable for electrical fittings. A plate of galalith $\frac{1}{12}$ inch thick, is impervious to a current of 16,000 volts. The sp.gr. is 1·317–1·35 (celluloid 1·34–1·40). The hardness is 2·5 (celluloid 2). It resists oily liquids and acids, but is swelled by alkaline liquids. Its chief drawback is its hygroscopic nature ; it absorbs 30 p.c. of its weight in 12 days. It is not elastic like celluloid, and breaks when slightly bent. On account of its tendency to flake it cannot be worked so well as celluloid, and sheets cannot be prepared less than 2 mm. in thickness (Bonwitt, l.c.).

Lactoform.— This is a patented preparation of casein resembling horn, giving, according to the specification, a hard and tough article which does not swell or materially soften when immersed in water. It is prepared by adding various salts to solutions of casein ; thus, by adding a solution of lead acetate to a solution of casein, a coagulum is produced from which lactoform, resembling *horn*, may be obtained, while to manufacture a substitute for ivory, carbonate of soda is added to the casein solution and precipitated by sugar of lead, thus forming carbonate of lead in the mass obtained. By the use of chromium compounds, bluish-green, also yellow and orange lactoform, is obtainable ; by the action of iron, rust-coloured, and in combination with tannic acid, slate and black-coloured, lactoform may be produced. These are merely intermediate products, and are not claimed as a new invention, but are converted into lactoform by treatment with formaldehyde.

For *glues* and *sizes*, casein is dissolved in borax, soda, or ammonia, and the resulting coating may afterwards be rendered insoluble by formaldehyde, or the casein may be dissolved in lime, which will give a waterproof coating when dry.

Films.—Schmidt has patented a process for making casein films as follows : 100 grams of casein are dissolved by heating in 1 litre of water containing 8 grams of 25 p.c. hydrochloric acid : 10 grams of 40 p.c. formaldehyde and a small quantity of glycerol are added, and the solution poured on glass plates to dry. He states that films made from alkaline solutions of casein are not impermeable to moisture.

Schmidt patents the following process : 100 grams of casein and 1·5 grams caustic soda are dissolved in 1 litre of water, to which are added about 15 grams of a 40 p.c. solution of formaldehyde ; or 100 grams of casein and 10 c.c. of a 10 p.c. solution of ammonia are dissolved in 2 litres of water, to which are added about 30 grams of a 40 p.c. solution of formaldehyde. Either of these he states, gives insoluble films on drying, which may be used for photography, surgical bandages, paper-coating, &c.

Buss, in his patent for photographic films, proceeds as follows : 500 to 700 grams dry casein are heated with 9 litres of water to 35° or 50°, mixed with 250 grams of citric acid dissolved in 1 litre of water, and the heating continued until the whole has dissolved. Then 100

or 200 grams of glycerol are added, and the liquid filtered It is applied by machine to plain or baryta paper, and allowed to dry. It is next rendered insoluble by being drawn through a 5 or 7 p.c. solution of ammonium or sodium chloride, and finally sensitised in a silver nitrate bath, ranging between 4 and 12 p.c. in strength.

Sealing for bottles.—For this purpose, Joirgnot has patented the following preparation : Casein is treated with a hot aqueous solution of sodium phosphate. ammonium fluoride and glycerol, the whole being then heated in the water bath until it is homogeneous and viscous. This product is employed for sealing bottles of metal, glass, porcelain, &c., by applying it in a warm state to the edge of the vessel or cover, and then treating it with formaldehyde.

Fining of wines.—For this purpose, a readily soluble sodium compound of casein is used. It is dissolved in 10 or 20 parts of water, the 5 p.c. solution effecting a somewhat slower though more complete clarification. The casein compound has the advantage that it is very much cheaper than albumen, and is free from all flavour such as is found in even the purest gelatin. Moreover, if in fining wines with white of egg, albumen or gelatin, too large an excess in proportion to the tannin be used, this excess remains in solution, and may lead to turbidity and alteration in the wine ; whereas the casein, even when added in considerable excess, is completely eliminated, being coagulated by the acid in the wine.

Casein water-paints.—Casein in fine powder is intimately mixed with sifted slaked lime and incorporated with the pigments The proportion of lime to casein is very important : if too little lime be used, the mixture will, after a short time, especially if exposed to air, become insoluble in water ; and if too much lime be used, adverse results will follow. The brushes will be rotted and the paint will be liable to flake off. The next matter of importance is the proportion of lime and casein to be incorporated with the pigment. If too little be used, the paint will dust off and will not stand washing ; and if too much be used, the coating will be brittle and flake off.

In selecting the pigments, it is necessary to employ only those which are unaffected by lime The most suitable are :

For White.	Whiting, China clay, zinc oxide.
„ Yellow.	Ochre, Hansa yellow, naphthol yellow, chrome yellow.
„ Brown.	Umber, sienna.
„ Black.	Carbon blacks.
„ Red.	Oxides, lithol red.
„ Blue.	Ultramarine.
„ Green.	Green earth, ultramarine green, lime green.

The ingredients must be thoroughly incorporated and kept in air-tight packages. The paint is prepared by mixing the powder with cold water, and is ready for use in a few minutes. When thoroughly dry, the surface is washable.

L. M. N.

CASHEW GUM *v.* Gums.

CASIMIROINE $C_{13}H_{14}O_6N_2(OMe)_2$, m.p. 196°–197°, and **casimiroedine** $C_{17}H_{24}O_5N_3$, m.p. 222°–223°, occur in minute amount in the seeds of *Casimiroa edulis* (La Llave et Lejarza) a reputed

Mexican drug. The alkaloids are physiologically inert (Power and Callan, Chem. Soc. Trans. 1911, 99, 1993, who give other references).

CASSAVA. The root of *Manihot palmata* (Muell.), ' sweet cassava ; ' or of *Manihot utilissima* (Pohl), ' bitter cassava.' These plants are widely cultivated in the tropics for the sake of their starchy edible roots. From them the substance tapioca is prepared. The starch is also known as mandioc starch, Brazilian, Bahia, Rio or Para arrowroot, and by other names.

The grains of starch are grouped in twos, threes, or fours ; the separate grains have usually one or two flat surfaces, but, on the whole, are rounded and show delicate concentric striations and a distinct hilum.

Cassava root contains a volatile poisonous substance (Fermin, 1761), which proved to be hydrocyanic acid (Boutron-Charlard, 1836, and Francis, Analyst, 1878, 2, 4). The latter observer found 0·0168 p.c. of prussic acid in sweet cassava root and 0·0275 p.c. in the bitter root. He found 59·4 p.c. and 61·4 p.c. water in the roots, and about 30 p.c. of starch.

Collens (Bull. Dept. of Agric. Trinidad and Tobago, 1915, 14, 54) found that the freshly-dug roots of the sweet and bitter varieties contain 0·0048 p c. and 0·053 p.c. of hydrocyanic acid respectively ; the leaves 0·0162 p.c. and 0 041 p c , and the peelings of the stems 0·043 p.c. and 0·113 p.c. respectively.

Leuscher (Zeitsch. öffentl. Chem. 1902, 8, 10), is the mean of six analyses of the fresh root, found :

Water	Protein	Fat	Starch	Sugar	Crude fibre	Ash
70·25	1·12	0 41	21·14	5·13	1·11	0 54

He states that the yield, on well-irrigated land, may amount to 15 or 16 tons per acre.

Tapioca is made from the starch of cassava by stirring the damp product on a hot iron plate until it agglomerates into the irregular, spherical masses familiar as tapioca. By this treatment, many of the starch grains become changed, being converted into shapeless, translucent masses.

According to American analyses (Wiley, Bull. 13, U.S. Dept. of Agric. Div. of Chem. 1898), tapioca contains -

Water	Protein	Fat	Carbohydrates	Fibre	Ash
11·23	0·37	0·03	88·16	0·12	0·09

Owing to the exceptionally low demands of cassava for mineral matter, it has been recommended as a crop particularly well adapted for cultivation on poor sandy soils, as it feeds very largely upon air and water (Ewell and Wiley, Amer. Chem. J. 1893, 15, 285). H. I.

CASSEL EARTH or **VANDYKE BROWN** *v.* Pigments.

CASSEL YELLOW. *Lead oxychloride.* A pigment also known as *Turner's Yellow, Montpelier Yellow, Mineral Yellow*, and *Patent Yellow.*

CASSELMAN'S GREEN. A pigment made by mixing boiling solutions of copper sulphate and an alkaline acetate.

CASSIA. The bark of *Cinnamomum cassia* (Blume), a tree belonging to the order *Lauraceæ* or true laurels. It is grown in China, Java, &c. *C. cassia* furnishes a bark which is much like cinnamon [*C. zeylanicum* (Nees)], but thicker, coarser, stronger, less delicate in flavour, and

cheaper; hence it is frequently used to adulterate cinnamon. The bark is stripped off the branches, when it rolls up in the form of quills. It is said to be preferred to cinnamon itself by some chocolate makers on account of its stronger flavour. The unopened flower-buds are also sold under the name of 'cassia-buds,' and possess similar properties to the bark. Other species of the genus afford aromatic barks, e q. C. culilawan (Blume), native of Malaya and China, the bark of which has a flavour of cloves; C. tamala (Nees), which occurs in sub-Himalayan India as far as Burma, and provides a bark that is used as a substitute for or adulterant of true cinnamon: C. Burmanni (Blume) is the source of the bark exported from Sumatra. The bark known as clove-cassia is obtained from Dicy pellium caryophyllatum (Nees), which is also a tree of the laurel family growing in Brazil.

The employment of cassia as a sophisticant of the more esteemed and more costly bark of cinnamon when in the ground state may usually be detected by adding tincture of iodine to a decoction of the powder; when, since cassia contains more starch than cinnamon, the substance will turn blue; but, where inferior qualities of the true cinnamon have been examined, their constitution has approached that of the coarser bark of cassia, and this test has proved uncertain (cf. O. Hehner, Analyst, 1879, 225–228).

Cassia bark is thicker, redder, stronger to the taste than cinnamon. The powder under the microscope exhibits a general resemblance to cinnamon, but it will be seen that cassia differs from cinnamon in its coarser structure, and especially in the greater size and number of its starch corpuscles.

Cassia yields by distillation an essential oil largely used in perfumery, especially for producing the scent in brown Windsor soap (v. OILS, ESSENTIAL).

CASSIA OIL v. OILS, ESSENTIAL.

CASSIA TORA (Linn.) or **TAGEREY-VEREY.** This plant produces grains known in the East Indies, Arabia, and Japan as Tora, but which are known in Pondicherry and other parts of Hindostan as Tagerey-verey. It is regularly used as a component of the indigo vat in dyeing, apparently serving the same purpose as the bran-madder or molasses used in Europe.

The native dyers use the Tagerey-verey in the following manner. To dye about 200 yards of cloth, 11¼ lbs. of the grain are steeped in from 5 to 6 gallons of cold water, and then boiled for four hours. The grains are swollen and softened by this treatment, and the water becomes thick and gummy. The whole of this is added to the indigo vat, and after standing for fifteen hours, the vat is ready to dye.

CASSITERITE or **TIN-STONE.** Native tin oxide, SnO_2, containing 78·6 p.c. of tin, and practically the only ore of the metal. It varies much in appearance—the colour ranges from white to black, being usually dark brown—and its most characteristic feature is its high sp.gr. of 6·8–7·1; hardness, 6–7, easily scratching glass. Crystals are tetragonal, with very characteristic knee-shaped twins; their faces are often very brilliant with an adamantine lustre. There is an absence of cleavage; and this readily helps to distinguish the mineral from blende.

Crystals are, however, not very common, the mineral being more frequently found as disseminated grains and water-worn pebbles. Grains of cassiterite in a concentrate panned from a river sand may be readily detected by a very simple characteristic test. When placed on a zinc plate, or in a basin with fragments of zinc, and dilute hydrochloric acid poured over, any grains of tin-stone soon show a shining white coating of metallic tin. Veins of tin ore usually occur at the junction of granitic masses and slates, and the ore also impregnates the rocks bordering the veins. Such ores are known as vein-tin, to distinguish them from the stream-tin of alluvial deposits. A compact variety with a radially fibrous and concentric structure and sometimes a botryoidal surface is known as wood-tin. The ore as prepared for market is known as black-tin, and in South America as barilla. The principal tin-producing countries are the Federated Malay States, the islands of Banka and Billiton in the Dutch East Indies, Siam, China, Australia (Queensland, New South Wales, Western Australia), Tasmania, Bolivia, Cornwall, and more recently South Africa (Transvaal and Swaziland), and Northern Nigeria. The production of tin ore amounts to about 100,000 tons per annum.   J. L. S.

CASSIUS, PURPLE OF, v. GOLD.

CASTILE SOAP v. SOAP.

CASTOR or **CASTOREUM.** (Bibergeil, Ger.) A name given to a secretion of the beaver (Castor fiber), contained in pear-shaped cellular sacs (found near the genital organs of the male and female animal), which are cut off and dried, to prevent the skin being affected by water. It is a substance analogous to civet and musk, and is of the consistency of thick honey and unctuous to the touch. The interior substance is solid, of a dark-brown or black colour. It has a faint smell, softens when heated, but becomes brittle when cold. When chewed, it sticks to the teeth like wax. It has a bitter acrid taste, and a fœtid, penetrating smell. Its fracture is shining, and when the substance is genuine it shows fragments of membrane indicating organic structure.

Three varieties are said to exist, the Russian, Bavarian, and American or Canadian, the first-named variety containing about 2 p.c. of the volatile oil, while the last contains only 1 p.c. Wöhler obtained phenic and benzoic acids and salicine from it. Lehmann found bile in a fresh sample together with alkaline urates, sebates, and an albuminoid substance. Laugier, Brandes, Batka, Bouillon Lagrange, and Hildebrant have also examined it. By extracting it with six times its weight of alcohol a colourless substance, castorin, has been isolated. Used in medicine and perfumery.

CASTOR OIL is obtained from the seeds of Ricinus communis (Linn.) and R. sanguineus.

The former plant appears to be indigenous to Africa (Egypt), but has been transplanted to India at a very early stage of history, so that some writers consider the plant indigenous to India itself. The plant grows in enormous quantities in all tropical and sub-tropical countries, and is even found wild to day in South America, notably in Paraguay and the Argentine.

The most important sources of castor seed

are East India, Java, the Mediterranean countries, Mexico, and the United States of America, whilst the cultivation of the plant has of recent years been developed in the Egyptian Sudan, Fiji, and the East African Protectorate.

In 1913 the imports of castor seeds into Marseilles amounted to 25,157 tons, as compared with 16,588 tons in 1912, and 11,509 tons in 1911 (Diplom. and Consular Reports, No. 5377 of 1914). By far the largest producer is East India.

The total imports of castor oil into this country in 1916 were 1,322,000 gallons ; in 1917 they were about 2,000,000 gallons. The imports of castor seed in 1917 were 45,000 tons, the bulk of which went to Hull, and yielded 4,176,000 gallons of oil, the greater part of which was used for aircraft engine lubrication (J. Soc. Chem. Ind. 1919, 20 R.).

The seeds consist of 20 p.c. of husks, which are rich in mineral matter, but contain no oil, and 80 p.c. of kernels, forming a white, softish mass. The whole seeds contain a toxic principle —'ricine' or ricinine. The kernels contain a powerful fat hydrolysing enzyme, which can be made use of on a manufacturing scale for hydrolysing oils and fats for soap-making purposes.

The enzymes lipase and esterase can be extracted from castor beans by means of ether (Falk and Sugiura, J. Amer. Chem. Soc. 1915, 37, 217). The lipase is capable of hydrolysing oils at temperatures as low as --5°, a fact which has an important bearing on the question of the enzymic hydrolysis of fats in food preserved in cold storage (Blanchet, Compt. rend. 1914, 158, 895). It is reversible in its action, and is capable of forming mono- di- and triolein from an emulsion of oleic acid and glycerol (Krausz, Zeitsch. angew. Chem 1911, 24, 829)

The seeds contain 46 to 53 p.c of oil. The oil is produced on a large scale either by expression or extraction. For the production of best quality oil—for medicinal purposes—the seeds are decorticated before being expressed. The press-cake is subjected to a second and third expression, but the oils so obtained are unfit for medicinal use, and are employed for technical purposes (soap-making, Turkey-red oil, and lubricating oils). The cakes retain the poisonous alkaloid, and are therefore unfit for feeding purposes. Although it is stated that by washing the cakes with 6 or 7 times their amount of a 10 p.c. sodium chloride solution, they can be freed from the alkaloid, no castor cake is actually used for feeding cattle, but applied exclusively to manuring the land. The extracted oil is only used for technical purposes.

Another method of removing the toxic principle is to grind the seeds with water into a thin paste, which is then poured into boiling water. This coagulates the proteins, and the solid matter when strained off and expressed leaves a meal with the following composition : Water, 9·2 ; ash, 7·3 ; oil, 2·6 ; proteins, 71·7 ; crude fibre, 5·0 ; and carbohydrates, 4·2 p.c. (Indian Trade J. 1908, 9, 309 ; 1909, 11, 273).

A simple physiological method of detecting castor seed in other seeds is described by Lander and Geake (Analyst, 1914, 39, 292).

Crude castor oil is refined by steaming the oil, whereby the albuminous substances are coagulated, so that they can be removed by filtering.

Castor oil is a colourless or pale-greenish oil, having a taste at first mild, then harsh ; this harsh taste is more pronounced in American than in Italian or French oils. The oil differs from all other fatty oils by its high specific gravity, viz. up to 0·968. Contrary to older statements, the oil does not dry, even when exposed to the atmosphere in thin layers. It has the following analytical characters : Sp.gr. 0 959–0·968 ; solidification point, —17° to —18° ; iodine value, 84–86 ; Reichert-Meissl value, 2 2·5 ; saponification value, 175–183 ; acetyl value, 150 , and m p of fatty acids, 13°.

Castor oil is strongly dextro-rotatory ; the optical activity is due to the presence of ricinoleic acid.

The chief constituent of castor oil is the triglyceride of ricinoleic acid, both isomerides ricinoleic and isoricinoleic acid being comprised under this term ; in addition thereto, castor oil contains a small proportion of glycerides of a natural dihydroxystearic acid and of stearic acid Palmitin and olein are absent.

Owing to the presence of triricinolein, castor oil is distinguished from all other fatty oils by its high 'acetyl value' (see above and OILS and FATS). Castor oil further differs from all other fatty oils by its ready miscibility with absolute alcohol and glacial acetic acid, as also by its insolubility in large quantities of light petroleum, kerosene, and high-boiling paraffin oils. The oil gives a homogeneous solution with an *equal* measure of light petroleum, or one volume and a half of kerosene or paraffin oil ; if more of the solvents is used, the excess will float on the top of the mixture. If castor oil be mixed with a small quantity of another fatty oil, this characteristic insolubility in petroleum distillates is lost.

On subjecting castor oil to destructive distillation (as in the preparation of 'cognac oil '), undecylenic acid and œnanthaldehyde distil over, whilst the residue solidifies to a very bulky, spongy, indiarubber-like mass, for which a solvent has not yet been found. This residue appears to consist of the anhydride of triundecenoic acid. By heating castor oil for 10 hours at a temperature of 260°–300° under a pressure of 4–6 atmospheres, the oil becomes miscible with mineral oils.

When heated at 150°–250°, and then neutralised with alkali, castor oil yields soaps which are soluble in hydrocarbons, &c. If, after heating, the oil is sulphonated before neutralisation, a substitute for Turkey-red oil is obtained, whilst evaporation of the product leaves a soap which does not readily form insoluble soaps with calcium and magnesium salts (Blumer, D. R. P. 227993, 1907 ; see also Eng. Pat. 24868, 1897).

Owing to its viscous character castor oil is particularly suitable for lubricating internal combustion engines, and is now largely used for aviation motors. Oil for this purpose should be colourless, have sp.gr. of 0·964–0·968, and an acid value of less than 0·3, and when heated in a flat dish for an hour at 215° should not darken to any material extent. The chief adulterants of oil supplied for lubrication are sugar and arachis oil (*q.v.*).

Castor oil is a good solvent for resins in

rubber, and may be used in the purification of raw rubber. The solution of extracted resins may be made into soap (Schopper, Gum. Zeit. 1916, 30, 601).

A process of preparing acidyl derivatives of castor oil, which are free from the objectionable odour and taste of the oil, has been patented (D. R. P. 226111, 1908). J. L.

CASTOR OIL SEEDS or CASTOR BEANS. The seed of *Ricinus communis*, a plant which grows as a tree in warm countries, attaining a height of 30 or 40 feet, but which in cooler climates is only an annual shrub.

The following is an analysis of Indian seeds (Halenke and Kling, Landw. Versuch. St. 1906, 64, 51) :—

	Sol carbo-Water Protein Oil hydrates Fibre Ash
Kernels, 70 p.c.	3·60 23·43 66·02 4·01 0·70 2·24
Husk, 30 p.c.	. 8·76 4·76 0·98 32·92 48·69 3·80
Whole seed	. 5·14 17·88 46·65 12·61 14·99 2·73

In many varieties the proportion of husk is much lower, sometimes down to 20 p.c.

Of the total 'protein,' 22·62 p.c., 4·18 p.c., and 17·13 p.c. respectively, are true albuminoids, whilst of the carbohydrates, 0 89 p.c., 15·63 p.c., and 5·29 p.c. respectively, are pentosans.

The ash of castor seeds was analysed by Thoms (1890)—

Sand,
Water etc Fe$_2$O$_3$ CaO MgO K$_2$O Na$_2$O P$_2$O$_5$ SO$_3$ Cl
0·30 19 59 5 65 17 08 10·53 14·30 1·88 23·67 6 01 0 29

Castor seeds are very poisonous. Cornevin found the following were the toxic doses in grammes per kilogram of body-weight. Horses, oxen, sheep and dogs, 3 ; pigs about 5–6 ; hens about 40.

The poisonous constituent was believed to be *ricinine* by Soane (Chem. Zentr. 1895, i. 853), but is now known to be *ricin*, an albumin, which, with two non-toxic substances—a proteose and a globulin—constitute the proteids of the seeds (Osborne and Mendel, Proc. Amer. Physiol. Soc. 1903, 36).

Ricinine, according to Macquenne and Philippe (Compt. rend. 1904, 138, 506 and 139, 840), has the composition C$_8$H$_8$O$_2$N$_2$; it melts at 201·5° and yields ricinic acid C$_7$H$_6$O$_2$N$_2$ by saponification. They represent its constitution as

$$\text{N(CH)}_3 \begin{array}{c} \text{C(COOCH}_3) : \text{C} \\ \\ \text{CH} = \text{CH} : \text{C} \end{array} \text{N}$$
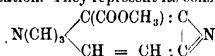
Ricin, the poisonous principle, has been examined by Stillmark (Chem. Soc. Abstr. 1890, 535), Osborne, and others (*l.c.* and Amer. Jour. Physiol. 1905, 14, 259), and Brieger (Chem. Zentr. 1904, i. 1286). It can be extracted from the pressed seeds by a 10 p.c. solution of common salt, from which it is precipitated by magnesium and sodium sulphates.

Ricin agglutinates the red corpuscles of the blood. Osborne found 0·002 milligram per kilogram of body weight sufficient to kill a rabbit when subcutaneously injected. It can be kept for months without deterioration, but loses its poisonous qualities when coagulated by heat Toxic symptoms do not appear until after a latent period, of about 15 hours. Castor seeds also contain an enzyme capable of decomposing fats into glycerol and fatty acids, or, according

to Falk and Sugiura (J. Amer. Chem. Soc. 1915, 37, 217), two enzymes—*esterase* and *lipase*, the former active towards ethyl butyrate, the latter towards triacetin. They also contain an enzyme *urease*, capable of hydrolysing urea (Falk, J. Amer. Chem. Soc. 1913, 1914, 36, 2166), similar to, but weaker than, the urease of soja beans.

Castor seeds are largely used as source of castor oil (*q.v.*). The cake left is rich in protein, and if it were not poisonous, would prove of value as a cattle food. It contains—

	Soluble			
Protein	Oil	carbohydrates	Fibre	Ash
29–34 p.c.	1–4 p.c.	12–18 p.c.	30–40 p.c.	6–9 p.c.

By subjecting the cake to high-pressure steam, the poisonous qualities are said to be destroyed, and cake so prepared may safely be used as a part of the ration of fattening animals. According to Ehrlich, animals may be immunised against the poison by feeding them with very small quantities of the crude cake until they become accustomed to it. The serum from such animals may then be used to immunise others.

Neither of these methods of utilising castor cake appears to have been successful, and, in England at least, it is rarely or never used for feeding purposes.

The leaves of the castor plant are rich in lime and potash : an analysis by Wayne (Pharm. J. Trans. 1874, 3, 749) gave as the composition of the ash of the leaves :—

CaO MgO K$_2$O Na$_2$O Fe$_2$O$_3$ P$_2$O$_5$ SO$_3$ Cl   CO$_2$ SiO$_2$
33·4 6·2 27·3 2·1   0·7   6 7 2·9   1·6 16·2 2·4
H. I.

CASUMEN. Trade name for a soluble form of casein.

CATALASE *v. Enzymes*, art. **FERMENTATION.**

CATALYSIS *v.* **CHEMICAL AFFINITY.**

CATAPLEIITE. Hydrated silicate and zirconate of sodium and calcium, containing ZrO$_2$ 30–40 p.c. The crystals are yellow and have the form of thin hexagonal plates ; sp.gr. 2·8, H. 6. It occurs with other rare minerals in nepheline-syenite on the islands in the Langesund-fjord in south Norway, and at Narsarsuk in Greenland. L. J. S.

CATECHU *v.* **CATECHU.**

CATECHOL (*Pyrocatechol* or *Pyrocatechin, o-Dihydroxybenzene*, 1 . 2-Phendiol C$_6$H$_4$(OH)$_2$), occurs in the leaves of the Virginia creeper (*Ampelopsis hederacea*) (Gorup Besanez, Ber. 1871, 4, 905) ; in the sap of various kinds of the kino plants (Eisfeldt, *ibid.* 906 ; Flückiger, Ber. 1872, 5, 1, 47) ; in crude beet sugar (Lippmann, Ber. 20, 3298 ; 1893, 26, 3061 ; J. Soc. Chem. Ind. 1893, 535) ; in the dry external scales of the onion ; in Paglia olive oil (Canzoneri, Gazz. chim. ital. 27, 3) ; in the colouring matter of red grapes (Sostegni, Gazz. chim. ital. 32, 17) ; in Silesian and Westphalian coal (Bornstein, Ber. 1902, 35, 4324) ; and in the tar water of bituminous shale (D. R. P. 68944, 1892 ; Ber. 1902, 35, 4325). The catechol complex also exists in certain glucosides (Nedra, J Soc. Chem. Ind. 1900, 686 ; Schmidt and Waljaschko, Chem. Zentr. 1901, ii. 121), in a large number of products of vegetable origin ; as the sulphate, catechol occurs in the urine of man and herbivorous animals (Müller, Ber. 1874, 7, 1526 ; Schmiedeberg, Zeitsch. physiol. Chem. 6, 189) ; it is probably also

contained in the cerebro-spinal fluid (Halli-burton, J. Phys. Chem. 10, 247).

It is formed in the dry distillation of mori-tannic acid (Wagner, Annalen, 1850, 75, 351, 80, 316); of catechin (Zwenger, Annalen, 1841, 37, 327); of protocatechuic acid (Strecker, Annalen, 1860, 118, 285), and of all tannins which give a green colouration with iron chloride (Uloth, Annalen, 1859, 111, 215). It is also formed when filter paper is heated to 200° or when starch or sugar is heated to 280° with water (Hoppe Seyler, Ber. 1871, 4. 15) and in many other reactions.

Catechol is prepared by fusing sodium o-benzene disulphonate (10 parts) with sodium hydroxide (10-15 parts) in an autoclave for 8-10 hours at 280°-300° and pressure of 2-3 atmospheres. The mass is then dissolved in dilute sulphuric acid, neutralised with chalk, evaporated, cooled and filtered. The mother liquor is now heated in an autoclave with 50 p.c. sulphuric acid (10 parts) to 180°-220°. The phenol is removed from the solution so obtained by blowing steam through it; it is then de-coloured with animal charcoal, after which the catechol is extracted with ether (Baum, Eng. Pat. 21853; D. R. P. 80817; J. Soc. Chem. Ind. 1894, 879; Ellis, ibid. 1897, 674; Frdl. 1894-7, 116). Catechol is also prepared by heating catechol disulphonic acid or the sodium salt with water or mineral acid to 200°-215° for 10-15 hours under pressure (Tobias, D. R. P. 81209, 1894; Frdl. 1894-7, 117); or by treating commercial catechu with water (Gutknecht, Chem. Zeit. 1891, 15, 959); or by diazotising o-aminophenol, treating the product with boiling aqueous copper sulphate, and then extracting the catechol with ether (Frdl. 1905-7, 128); or by the distillation of orthobromo- or chloro-phenol in vacuô or in steam (D. R. P. 76597; Frdl. 1890-4, 845), or by heating with sodium hydroxide (Frdl. 1894-7, 114; D. R. P. 84828). An almost theoretical yield of catechol can be obtained by treating guaiacol with fuming hydriodic acid (Perkin, Chem. Soc. Proc. 1890, 90); or by the interaction of o-hydroxybenzalde-hyde with aqueous sodium hydroxide in equi-molecular proportions; to the sodium salt thus formed, an equimolecular proportion of 2-3 p c. hydrogen peroxide is then added and the catechol is extracted with a suitable solvent (Dakin, Amer. Chem. J. 1909, 42, 477). Also formed, together with phenol, by acting on benzene with hydrogen peroxide in presence of a ferrous salt. Other methods of preparing catechol are described by Cross, Bevan, and Heiberg (Ber. 1900, 33, 2018); Kunzkrause (Ber. 1897, 30, 1620); Meyer (ibid. 2569); Hart-mann and Gattermann (Ber. 1892, 25, 3532; D. R. P. 70718; Frdl. 1890-4, 52); Gilliard, Monnet and Cartier (D. R. P. 97099; Chem. Zentr. 1898, ii. 521); Messel (D. R. PP. 68944, 60637; Frdl. 1890-4, 844, 846).

Catechol is readily soluble in water, alcohol, ether, benzene, and crystallises from these solvents in prismatic needles or tablets; m.p. 104°; b.p. 245° (Gräbe, Annalen, 1889, 254, 296). Its aqueous solution precipitates metallic silver from silver nitrate solution at ordinary temperature, and with ferric chloride it gives a green colouration, which turns violet on addition of ammonia or sodium acetate (Wislicenus,

Annalen, 1896, 291, 174), whilst in the presence of aromatic amino-sulphonic acids the colour changes to red-brown and the test is more delicate than with ferric chloride alone (Bayer, Biochem. Zeitsch. 1909, 20, 178). Unlike its isomeride, resorcinol (metadihydroxybenzene), it is converted into an unstable quinone by the action of silver oxide, and its calcium salt $Ca(C_6H_8O_2)_2$ is precipitated by an ammoniacal solution of calcium chloride (Böttinger, Ber. 1895, 28, Ref. 327). Catechol can be separated from its isomeride by adding antimony fluoride to their aqueous solution, when only catechol antimonyl fluoride will be precipitated (Causse, Ann. Chim. Phys 1898, (vii.) 14, 526, 538).

An alkaline solution of catechol becomes green, then black on exposure to air; cate-chol is also oxidised to a black insoluble sub-stance by the action of Catecholase, a thermo-stable substance obtained from the young shoots of Salix purpurea (Weevers, Proc. K. Akad. Wetensch, Amsterd. 1909, 12, 193). Heated with ammonium carbonate to 140°, catechol yields protocatechuic acid $C_6H_3(OH)_2CO_2H$.

Catechol is used in photography, forming a very efficient developer in the presence of sodium sulphite or tribasic sodium phosphate as accelerator (Eder, J. Chem. Soc. Ind. 1890, 102; Brit. J. Photogr. 1900, 47, 676). It can also be used as the starting-point in the prepara-tion of a large number of valuable derivatives.

Alkali salts of catechol of the general com-position $OH·C_6H_4·OM,C_6H_4(OH)_2$, can be ob-tained by treating catechol with a solution of the theoretical quantity of alkali hydroxide or of a salt with an alkaline reaction, such as the sulphites. They form readily crystallisable salts, used in photography, and can be employed for producing pure catechol (Meister, Lucius and Brüning, D. R. P. 164666, 1904; Frdl. 1905-7, 129).

The mono- and di-ethyl ethers of catechol are prepared by heating under pressure a solu-tion containing catechol, sodium hydroxide, and sodium ethyl sulphate or chloride in equivalent proportions. The ethers are then removed by steam distillation and separated by treatment with sodium hydroxide, in which only the mono-ether is soluble (J. Soc. Chem. Ind. 1896, 741; Eng. Pat. 16047, 1896). The diethers can be pre-pared by the action of alkalis on the monoethers (Frdl. 1894-7, 123; D. R. P. 92651).

Catechol monoethyl ether forms large clear colourless crystals, m.p. 26°-27°, b.p. 215°, which have an odour similar to that of thymol, and are soluble in alcohol and ether, but not in water.

The monoalkyl ethers of catechol, when fused or treated in solution with various proteids, albumoses, and peptones, yield compounds which are applied therapeutically (Fehrlin, D. R. P. 162656, 1906).

Monoethyl catechol ether v. GUAIACOL.
*Dimethyl catechol ether v.* VERATROL.

Catechol, when fused with aliphatic amines or heated with them in suitable solvents, yields stable amines which form useful photographic developers (D. R. P. 141101, 1903; Frdl. 1900-2, 1218). Other amino- and also nitro-derivatives are described by Meldola, Woolcott and Wray (Chem. Soc. Trans. 1896, 1332); Heinisch (Monatsh. 1894, 15, 229); Nietzki and

Moll (Ber. 1893, 26, 2182); Blankswa (Rec. trav. chim. 1905, 24, 40); Grischkewitsch-Trochimowski (J. Russ. Phys. Chem. Soc. 1909, 41, 1324); Dakin (l.c.).

Good stable black, greenish, and bluish-black dyes, soluble in carbonates and alkaline sulphides, have been obtained by the action of aliphatic amines on catechol at 180°–222° (D. R. P. 84632; Frdl. 1894–7, 1048).

Methylene catechol ether $CH_2 \langle {}^O_O \rangle C_6H_4$ is a colourless liquid; b.p. 172°–173° (Moureu, Bull. Soc. chim. 1897, 15, 654; Mameli, Atti. R Accad. Lincei, 1906, (v.) 15, ii. 101; Perkin, Robinson, and Thomas, Chem. Soc. Trans. 1909, 1977). A number of derivatives have been prepared (Moureu, l.c. 1898, 19, 507; Medinger, Monatsh, 1906, 27, 237; Barger, Chem. Soc. Trans. 1908, 563, 2081; Barger and Ewins, ibid. 735).

Catechol diphenylmethylene ether

$$CPh_2 \langle {}^O_O \rangle C_6H_4$$
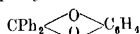
is prepared by gently heating catechol with benzophenone chloride; colourless prisms, m.p. 93° (Sachs and Thonet, Ber. 1904, 37, 3327).

The methylene ethers of catechol derivatives can be converted into chlorine derivatives of their cyclic carbonates by being heated with thionyl chloride (Wellcome and Barger, Eng Pat 15987, 1907; J. Soc. Chem. Ind 1908, 355).

Catechol ethylenic ether $C_6H_4 \langle {}^{O \cdot CH_2}_{O \cdot CH_2}$ b p. 216° (110°–111°, 31 mm.), is readily obtained by heating catechol with potash, ethylenic bromide and water in an atmosphere of hydrogen. Potassium permanganate, hydrogen iodide, and ammonia have an action on it, but it is oxidised by chromic acid to oxalic and carbonic acids. It yields a number of substitution derivatives (Moureu, Compt. rend. 1898, 126, 1426; Bull. Soc. chim. 1898, (iii.) 19, 507; Gattermann, Annalen, 1907, 357, 313; Lazennec, Bull. Soc. chim. 1909, (iv.) 5, 501, 509).

Catechol acetylenic ether $C_6H_4 \langle {}^{O \cdot CH}_{O \cdot CH}$ is prepared by dehydrating orthohydroxyphenoxyaldehyde with phosphoric anhydride in presence of quinoline. It is a colourless oil, boiling at 193°, and, when strongly cooled, forms brilliant white crystals, m.p. 16°–20°. It forms a dibromide $C_6H_4O_2(CH)_2Br_2$, m.p. 103°–104·5°, which, in contact with water, is converted into catechol, glyoxal, and hydrogen bromide (Moureu, Compt. rend. 1899, 128, 559).

Catechol forms a number of *acetals* (Moureu, Compt. rend. 1898, 126, 1656); also a vinyl derivative (Kurz Krause, Ber. 1897, 30, 1617; Pauly and Neukam, ibid. 1908, 41, 4151).

Catechol sulphonic acid $C_6H_3(OH)_2SO_3H$ is conveniently prepared by stirring together a meta-halogen phenol sulphonic acid with about an equal weight of sodium hydroxide in aqueous solution, and heating the mass to 250° for 8–10 hours. The mass is now dissolved in water and neutralised with a mineral acid such as sulphuric. The solution is evaporated and the sodium sulphate filtered off, whilst the concentrate solution of catechol sulphonic acid yields

pure catechol when heated with mineral acids (Frdl. 1897–1900, 150; 1902–4, 100; D. R. P. 9623; Ellis, Eng. Pat. 14931, 1896).

Catechol disulphonic acid is obtained by treating catechol with 5 times the amount of fuming sulphuric acid (Cousin, Compt. rend. 1893, 117, 113), or by fusing phenol trisulphonic acid or its salts with alkalis and decomposing the alkali sulphonate so obtained with dilute sulphuric acid (Frdl. 1894–7, 118).

Halogen derivatives (Jackson and Boswell, Amer Chem. J. 1906, 35, 519; Dakin, l.c.).

Monochlorcatechol $C_6H_3(OH)_2Cl$, m.p. 80°–81°, is obtained by the interaction of sulphuryl chloride with catechol in ethereal solution; by using a larger proportion of sulphuryl chloride, the *dichlorcatechol*, m.p. 105°–106°, is obtained (Paratoner, Gazz. chim. ital. 1898, 28, i. 197).

Trichlorcatechol $C_6H_3Cl_3O_2$ is obtained by the action of a chlorine solution in acetic acid or an acetic chloroform solution on catechol. It forms colourless odourless prisms, m.p. 104°–105°, with a burning taste. Excess of chlorine yields *tetrachlorocatechol* (Cousin, Compt. rend. 1895, 120, 840). The corresponding bromoderivatives are obtained similarly (Cousin, l.c.).

The bismuth brominated catechols are recommended as a satisfactory substitute for tribromphenoxide, which is employed medically, under the name of 'xeroform.' They are produced by adding an acid solution of bismuth nitrate to alkaline, tetra-, tri-, or di-bromocatechol, or by introducing precipitated bismuth hydroxide into an alcoholic solution of the bromocatechol (D. R. P. 107544, 1909).

Catechol carboxylic acid

$$C_6H_4(OH) O \cdot CO_2H, \tfrac{1}{2}H_2O$$
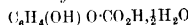
m.p. 240°, is formed by the action of ammonium carbonate on catechol at 130°–140° under pressure, or by heating catechol with glycerol and potassium hydrogen carbonate at 180°–210° in an atmosphere of carbon dioxide (Praxmarer, Monatsh. 1906, 27, 1199). The *di-carboxylic acid* can also be prepared. Derivatives of catechol carboxylic acid, used in medicine, are obtained by the interaction of alcohols and also of primary and secondary bases with catechol carbonate; thus:

$$C_6H_4 \langle {}^O_O \rangle CO + C_2H_5OH$$
$$= C_6H_4(OH)O \cdot CO_2C_2H_5$$
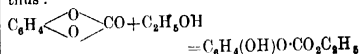
or by using aniline, the compound $C_6H_4(OH)O \cdot CONHC_6H_5$ is obtained, whilst with ethylene diamine it forms dicatechol-dicarbethylenediamine $C_2H_4(NH \cdot CO_2C_6H_4 \cdot OH)_2$ (Einhorn and Lindenberg, Annalen, 1898, 300, 135; D. R. P. 92535; Frdl. 1894–7, 1110). A number of similar compounds are described by Einhorn and Lindenberg (l.c.); Einhorn and Pfeiffer (Annalen, 1898, 310, 218).

Methyl catechol dicarbonate, m.p. 41°, is described by Syniewski (Ber. 1895, 28, 1874).

Carbonyl esters of catechol of the type $CO(OC_6H_4OR)_2$, also used in medicine, are prepared by the action of phosgene on, the corresponding alkyl catechol in sodium hydroxide solution (D. R. P 72806; Frdl. 1890–4, 854).

¶*Catechol monoacetic acid*

$$C_6H_4(OH)O \cdot CH_2 \cdot CO_2H$$
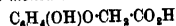
m.p. 131°, is obtained by the action of monochloracetic acid on catechol in aqueous or alkaline solution. When heated to 120°, it forms the anhydride $C_6H_4\stackrel{OCH_2}{\underset{O}{<}}CO$, m.p. 56° (J. Soc. Chem. Ind. 1896, 588), which, when treated with water, yields the acid in a very pure state (D. R. PP. 87336, 87668, 87669, 89593; Frdl. 1894–7, 1106, 1107, 1108). The sodium salt of this acid is said to be a better remedy for phthisis and loss of appetite than guaiacol or its carbonate (Frdl. 1894–7, 1106). A large number of derivatives formed by the acid are described by Ludwig (J. pr. Chem. 1900, ii. 61, 345). *Catechol diacetates* are described by Drczgowski (J. Russ. Phys. Chem. Soc. 25, 157), and by Voswinckel (Ber. 1909, 42, 4561).

Catechol reacts with chloracetyl chloride or chloracetic acid, forming *chloroacetyl catechol*, thus:

$$C_6H_4(OH)_2 + ClCH_2 \cdot COCl = C_6H_3(OH)_2 CO CH_2Cl$$
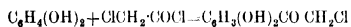
which, with ammonia or a primary aliphatic amine, yields amino-acetyl compounds of the type $RNHCH_2CO C_6H_3(OH)_2$, and these ketocompounds can be readily reduced to the corresponding alcohol (Imray, Eng. Pat. 26480, 1903; J. Soc. Chem. Ind. 1904, 1043; D. R. P. 13209; Frdl. 1890–4, 857) (*see also* ADRENALINE).

Aniline and chloroacetyl catechol form an *anilide* $C_6H (OH)_2 CO \cdot CH_2 \cdot NHPh$, which, with nitrous acid, yields *catecholglycophenyl triazine* $[C_6H_3(OH)_2]_2 CO CH_2 \cdot N \cdot Ph N \cdot NCH_2CO$; m.p. 115°, with decomposition. The corresponding *tolyl-* derivative melts at 120°, and is prepared in a similar manner (Dzierzgowsky, Ber. 1894, 27, 1983; D. R. P. 71312; Frdl. 1890–4, 857).

Acetocatechol $C_6H_3Ac (OH)_2$, m.p. 116°; *di-methoxyacetcatechol* $C_6H_3Ac.(OMe)_2$, and *catecholglycothiocyanate* $C_6H_3(OH)_2 CO \cdot CH_2 \cdot SCN$, m.p. 147°–150°, have been prepared by Dzierzgowsky (*l.c.*). According to Abderhalden and Kautsch, the chloracetyl derivatives of catechol, when treated with ammonia, are resolved into their components (Chem. Zentr. 1910, ii. 1356).

Alkyl acetyl catechol alkyl ethers, used in pharmacy, are obtained by the action of the alkyl acetyl chlorides on catechol monoalkyl ethers (J. Soc. Chem. Ind. 1906, 653; Eng. Pat. 25571, 1905; U.S. Pat. 822339, 1906).

A soluble tasteless product, $C_{10}H_8N_2O_6$, useful for medical purposes and as a substance from which other valuable technical products can be obtained, is formed by the condensation of catechol with alloxan in the presence of zinc chloride or mineral acids. It forms prismatic crystals, which decompose above 200° (D. R. P. 107720; Frdl. 1897–1900, 964).

Catecholdiantipyrine is obtained by mixing aqueous solutions of its constituents, and forms colourless needles; m.p. 78°–79° (Paten and Dufan, Compt. rend. 1895, 121, 532).

Piperidine catechol $C_5H_{11}N_1[C_6H_4(OH_2]_2$ forms white crystals which rapidly become red and then brown on exposure to air. It melts at 80°–81° (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 140).

Catechol, when treated with phthalic anhydride and sulphuric acid at 150°, yields alizarin, thus:

$$C_6H_4\stackrel{OH(1)}{\underset{OH(2)}{<}} + C_6H_4\stackrel{CO}{\underset{CO}{<}}O$$
$$= C_6H_4\stackrel{CO}{\underset{CO}{<}}C_6H_2\stackrel{OH(1)}{\underset{OH(2)}{<}}$$
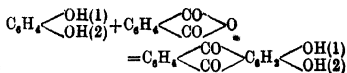
(Baeyer and Caro, Ber. 1874, 7, 972; Liebermann and Hohenemser, *ibid.* 1902, 35, 1778) (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

Catecholphthalein $C_{20}H_{14}O_6$ is prepared by heating phthalic anhydride (3 parts) with catechol (2 parts) and zinc chloride (3 parts) to 140°–150° for 3–4 hours. The aqueous extract of the product is boiled with animal charcoal, and the filtrate, on cooling, deposits yellowish-white leaf crystals of the substance which sinters 80°–90°, but does not melt (Meyer and Pfotenhauer, Ber. 1907, 40, 1442; Bayer, Chem. Zentr. 1910, ii. 1524).

Under certain conditions, catechol combines energetically with diazo- compounds yielding azo-dyes (Witt and Mayer, Ber. 1893, 26, 1072; Orton and Everatt, Chem. Soc. Trans. 1908, 1021). Thus *Benzeneazocatechol* $C_6H_3(OH)_2N_2C_6H_5$, m.p. 165°, which dyes cotton mordanted with alumina a golden yellow, is formed by the interaction of an alcoholic solution of catechol and a concentrated solution of diazobenzene chloride, the mixture then being poured on to ice. The *nitro-* derivative $NO_2 \cdot C_6H_4N_2C_6H_3(OH)_2$ colours alumina mordants red, and iron and chromium mordants brown; the sodium sulphonate $SO_3Na C_6H_4N_2C_6H_3(OH)_2$ colours wool mordanted with alumina, yellow; with chromium, red-brown. Similar toluene compounds have also been obtained. Catechol also forms triazo- or azonido- compounds (Rupe and Majewski, Ber. 1900, 33, 3401).

Catechol glycoisoquinoline

$$HO \cdot C_6H_3\stackrel{CO \cdot CH_2}{\underset{O - NC_9H_7}{<}}$$
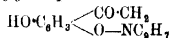
forms glittering orange-coloured crystals which give a red colouration with very dilute ferric chloride and a green colour in presence of excess of the latter; both the base and the chloride dye cotton mordanted with iron, aluminium, or chromium salts, black-yellow or reddish-brown respectively (Nencki, Ber. 1894, 27, 1969).

Catecholglycotetrahydroquinoline $C_{17}H_{17}NO_3$ crystallises in yellow lustrous plates; m.p. 170° (Nencki, *l.c.*).

Catechol, when heated with zinc chloride and formic acid, yields *aurin* dyes which give fast colours with metallic oxide mordants (Caro, Ber. 1893, 26, 254).

Catechol tannins are employed in colouring leathers (J. Soc. Chem. Ind. 1907, 423, 882; *ibid.* 1909, 1151).

A number of products obtained by the condensation of catechol with ketones are described by Fabinyi and Széky (Ber. 1905, 38, 2307).

Catechol, when warmed with an alcoholic solution of picryl chloride containing sodium, yields 3 : 5-*dinitro-o-diphenylene oxide*, $C_6H_4O_2 \cdot C_6H_2(NO_2)_2$, m.p. 192°–192·5° (Hillyer, Amer. Chem. J. 1900, 23, 125).
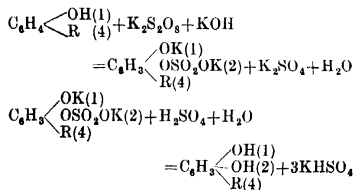
Catechol heated with hippuryl chloride on the water-bath yields *o-hydroxyphenyl hippurate* $NHBz \cdot CH_2 \cdot CO_2C_6H_4 \cdot OH$, m.p. 134°–136°, which with hydrogen chloride gives the anhydride $C_{16}H_{13}O_3N$, m.p. 232°–233° (Fischer, Ber. 1905, 38, 2926).

When catechol is hydrogenated in the presence of finely divided nickel, cis-cyclohexane 1 : 2-diol, m.p. 75°–76°, b.p. 225°, is formed (Sabatier and Mailhe, Compt. rend. 1908, 146, 1193).

A number of quinone and halogen quinone derivatives of catechol are described by Jackson and Koch (Amer. Chem. J. 1901, 26, 10); Jackson and Porter (ibid. 1903, 30, 518); Jackson and Russe (ibid. 1906, 35, 154 ; Ber. 1905, 38, 419). Other derivatives of catechol have also been prepared (Cousin, Ann. Chim. Phys. 1898, (vii.) 480 ; 1899, (vii.) 18, 76 ; Bischoff, Ber. 1900, 33, 1669 ; Wisinger, Monatsh. 1900, 21, 1007 ; Bischoff and Hedenström, Ber. 1902, 35, 3452 ; Bischoff and Fröhlich, Ber. 1907, 40, 2779, 2790 ; Barger and Ewins, Chem. Soc. Trans. 1909, 552, 1482 ; Fourneau, J. Pharm. Chim. 1910, (vii.) 1, 55, 97).

Catechol phosphines and chlorophosphines (Krauer, Ber. 1894, 27, 2565); phosphites and sulphites (Anschütz and Posth, Ber. 1894, 27, 2751); also a number of antimonyl catechol compounds (Causse, l.c.), some bismuth derivatives (Richard, Chem. Zentr. 1900, ii. 629), and a lead salt (Jackson and Koch, Ber. 1898, 31, 1458), have been prepared.

Homologues of catechol, such as homocatechol (o-dihydroxytoluene), can be prepared by heating the corresponding alcohol with catechol in the presence of zinc chloride in open or sealed vessels (Merck, Frdl. 1894–7, 115, D. R. P. 78882), or by the interaction of persulphates and p-phenol derivatives in alkaline solution, the product then being warmed with acid (Frdl. 1894–7, 121 ; D. R. P. 81298).

$$C_6H_4{<}^{OH(1)}_{R\ (4)}+K_2S_2O_8+KOH$$

$$=C_6H_3{<}^{OK(1)}_{\ OSO_2OK(2)}_{R(4)}+K_2SO_4+H_2O$$

$$C_6H_3{<}^{OK(1)}_{\ OSO_2OK(2)}_{R(4)}+H_2SO_4+H_2O$$

$$=C_6H_3{<}^{OH(1)}_{\ OH(2)}_{R(4)}+3KHSO_4$$

This method can be applied to the production of a large number of various derivatives.

CATECHU or **CUTCH.** There are several varieties of catechu or cutch bearing different names according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners : Gambier catechu, Bengal or Acacia catechu, Bombay or Areca catechu, and Mangrove cutch.

Although catechu has perhaps received greater attention than other natural dyes, the results have been so varied that the chemistry of the subject was for a long time in a most unsatisfactory condition. Some confusion has arisen from the non-appreciation of the fact that the main constituents of Gambier and Acacia catechu are not identical, and some uncertainty has also apparently existed as to the botanical origin of the commercial varieties. Bombay catechu is, for instance, occasionally referred to as originating from the *Acacia catechu*, and *Bengal catechu* from the *Areca catechu* (Linn.); and in many cases, at the present time, it is impossible

to ascertain the botanical derivation of commercial brown cutch preparations.

Gambier catechu.—Gambier, yellow cutch, cubical cutch, cube gambier, or terra japonica, is obtained from the *Uncaria gambier*, an extensive scandent bush which is met with, both wild and cultivated, in Malacca, Penang, and Singapore. The catechu is isolated by extracting the leaves and twigs with hot water until the liquid becomes syrupy, the insoluble matter being removed from time to time by means of a strainer. On cooling, the pasty mass is cut into cubes with sides 1 inch in length and dried on bamboo trays.

Catechin $C_{15}H_{14}O_6,4H_2O$, the crystalline principle, was first described by Nees van Esenbeck (Annalen, 1832, 1, 243), was subsequently examined by Berzelius in 1837 (J. 14, 235), and more recently by numerous chemists. To isolate catechin, Löwe (Zeitsch. anal. Chem. 13, 113) devised the following method : catechu is washed with cold water to remove catechu tannic acid, well pressed, allowed to dry, and dissolved in hot acetic ester. The filtered solution is evaporated and the residue crystallised from hot water.

According to Perkin and Yoshitake (Chem. Soc. Trans. 1902, 81, 1162), a combination of this method and that of Berzelius (l.c.) gives good results.

The finely powdered catechu is extracted with 10 times its weight of boiling ethyl acetate, the solution is evaporated, and the residue crystallised from 10 times its weight of water. The product is again dissolved in boiling water, and lead acetate solution added, drop by drop, until a coloured precipitate is no longer formed, and the filtrate is almost colourless ; the latter, while hot, is treated with sulphuretted hydrogen, the lead sulphide removed, and the crystals, which separate on cooling, are collected, washed, and allowed to dry at the ordinary temperature. The substance is now practically colourless, and the yield greater than if the purification had been effected by frequent crystallisation from water.

The formulæ which have been assigned to catechin are very numerous. It has been shown by v. Kostanecki and Tambor (Ber. 1902, 35, 1867), and simultaneously by Perkin and Yoshitake (l.c.), that it is correctly represented as $C_{15}H_{14}O_6,4H_2O$.

Catechin forms colourless needles, and when crystallised from water the air-dry product melts at 96° (Clauser, Ber. 1903, 36, 101). After standing over sulphuric acid, it possesses the formula $C_{15}H_{14}O_6,H_2O$, and melts at 176°–177°, and this is also the melting-point of the anhydrous substance. Catechin is readily soluble in boiling water and cold alcohol, and gives with lead acetate solution a colourless precipitate, and with ferric chloride a deep-green liquid. With pine wood and hydrochloric acid, it gives the phloroglucinol reaction.

On fusion with alkali, *protocatechuic acid, phloroglucinol*, and probably acetic acid are produced, and it is interesting to note that catechu has been considerably employed for the commercial preparation of the former compound.

Schützenberger and Rack (Bull. Soc. chim. 4, 6) have described a dibenzoylcatechin ; and Liebermann and Tauchert (Ber. 1880, 13, 695),

diacetyl catechin, diacetyl dichlorcateohin, and diacetyl dibromcatechin ; but their formulæ for these compounds are now known to be incorrect.

Penta - acetyl - catechin $C_{15}H_8O_6(C_2H_3O)_5$; colourless needles, m.p. 124°-125° (v. Kostanecki and Tambor) ; *pentabenzoyl catechin,* $C_{15}H_9O_6(C_7H_5O)_5$, colourless needles. m.p. 151°-153° ; *tetrabenzoyl catechin,* $C_{15}H_{10}O_6(C_7H_5O)_4$; prisms, m.p. 171°-172° (Perkin and Yoshitake) ; *disazobenzene catechin,* $C_{15}H_{12}O_6(C_6H_5N_2)_2$, salmon - red needles, m.p. 193°-195° (Etti, P. and Y.) ; *acetyldisazobenzene catechin,* orange red needles, m.p. 253°-255° (P. and Y.) ; *catechin tetramethylether* $C_{15}H_{10}O_2(OCH_3)_4$, needles. m.p. 141°-146° (K. and T.), *acetyl catechin tetramethylether* $C_{15}H_9O_2(OCH_3)_4C_2H_3O$, needles, m.p. 92°-93°, and *catechin pentamethylether* $C_{15}H_9O(OCH_3)_5$ (K. and T.), have been prepared.

When catechin tetramethylether, suspended in water, is oxidised with potassium permanganate, it gives *veratric acid,* and most probably *phloroglucinol dimethylether* (Chem. Soc. Trans 1905, 87). As the result of this investigation, Perkin considered that catechu was possibly a reduction product of quercetin :

or
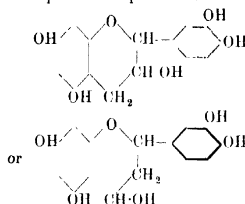
and indeed a small quantity of the latter colouring matter is present in catechu (Löwe. Perkin, *ibid.* 71, 1135).

More recently, v. Kostanecki and Lampe (Ber 1906, 39, 4007) have shown that when catechin tetramethylether is brominated in the presence of sunlight, only a *monobromcatechin tetramethylether,* m.p. 173°-174°, is produced, whereas the above constitutional formulæ require the formation of a dibromo- compound. When oxidised with permanganate, bromcatechin tetramethylether gives veratric acid, so that the bromine must have replaced one hydrogen of the phloroglucinol nucleus. When alcoholic solutions of catechin-tetramethylether and of iodine and iodic acid are mixed, long colourless needles of *iodocatechin-tetramethylether* separate after a few hours :—
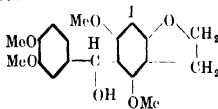

m.p. 192°-193° ; this yields an *acetyl derivative* $C_{21}H_{23}O_7I$, m.p. 189°.

Iodocatechin-tetramethylether when treated with zinc-dust and alkali yields the original catechin-tetramethylether, this elimination of iodine being also noticed with other members of the maclurin type (v. Kostanecki and Lampe, Ber. 1907, 40, 4910). v. Kostanecki and Lampe
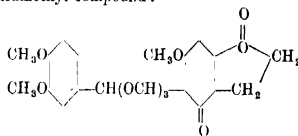
have assigned the following constitution to catechin :—
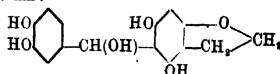
and this is in harmony with many of the properties of this substance. When catechin tetramethylether is oxidised with chromic acid, *catechone trimethylether,* orange-yellow needles, m.p. 210°, is produced (K. and T.) ·
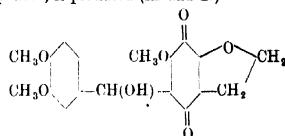
whereas catechin pentamethylether gives the tetramethyl compound :

and this behaviour is analogous to that of leucomaclurin pentamethylether (*see* MACLURIN).

Acetyl catechone by reduction with zinc-dust and glacial acetic acid, and hydrolysis of the product, gives *hydroxy-catechin,* yellow needles, melting at 284°-285°—
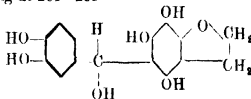

The hexamethylether has m.p. 102° (Nierenstein, Annalen, 1903, 396, 194).

When catechone trimethylether is nitrated, a mononitro- derivative.(1) :
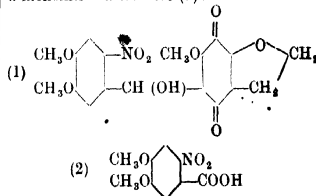
m.p. 141°, is obtained, and on oxidation yields nitroveratric acid (2). Finally, by the reduction of catechin tetramethylether with sodium and alcohol, an oil is produced which, on treatment with methyl sulphate, gives *pentamethoxyethyldiphenylmethane*
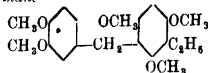

a reaction which points clearly to the presence of the cumaran ring in catechin.

Ryan and Walsh (Proc. Roy. Dub. Soc.

1916, 15, 113) have attempted to decide between the chroman structure of Perkin and Yoshitake and the coumaran formula of v. Kostanecki and Lampe. To this end they have synthesised 2 : 4 : 6 : 3′ : 4′-penta-methoxy-3-ethyl-diphenyl-methane, in order to ascertain whether this was identical with the deoxy-hydro-catechin-penta-methyl-ether obtained from catechin, as described above by v. Kostanecki and Lampe.

The synthesis is made clear by the following scheme :—
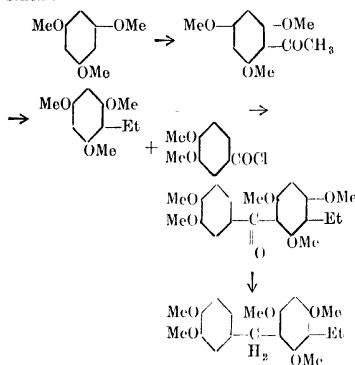
They were, however, unable to obtain the resulting product in a crystalline condition—the addition of a crystal of the product obtained from catechin (deoxy-hydro-catechin-penta-methyl-ether) failed to cause it to crystallise —hence they were not able to obtain a definite settlement of this point.

Catechin is oxidised in aqueous solution by potassium ferricyanide in the presence of potassium acetate with formation of an orange-coloured amorphous compound (Perkin), which dyes mordanted calico orange-brown shades which are fairly fast to soap. It is probable that this dyestuff is related to the catechone of v. Kostanecki and Tambor, and which was obtained by these authors in the form of its tri- and tetramethyl ethers.

When catechin is treated with carbon tetrachloride and aqueous potassium hydroxide, it yields *catechin carboxylic acid*, colourless needles, m.p. 274°-277° (decomp.) :—

$$COOH \cdot C_6H_2(OH)_2 - CH(OH) - \underset{OH}{\overset{HO}{\diagdown}} \overset{O}{\underset{}{\diagup}} \overset{CH_2}{\underset{CH_2}{}}$$
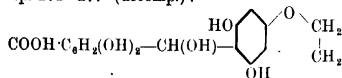
The annexed constitution has been assigned to it on account of the fact that its *penta-methyl-ether methyl-ester* $C_{22}H_{26}O_8$, m.p. 92°, when oxidised with alkaline permanganate, yields hemipinic acid.

Catechin carboxylic acid has been resolved, and the *d*-acid has $[\alpha]_D^{18} = +76.4°$, and m.p. 273° (decomp.), whilst the *l*-acid gave values $[\alpha]_D^{18} = -68.22°$, and m.p. 270°-273° (decomp.) (Nierenstein, Annalen, 1913, 396, 194).

Catechutannic acid. In addition to catechin,

gambier scatechu contains a small amount of catechutannic acid, and this substance is present in considerable quantity in the browner varieties of cutch. To isolate it, the following method has been employed :—

A hot aqueous extract of catechu is allowed to stand until no more catechin is deposited, and the clear liquid is evaporated to dryness. The residue is dissolved in alcohol, the solution treated with ether to precipitate impurities and then evaporated to dryness.

Catechutannic acid consists of an amorphous reddish-brown powder, readily soluble in water and alcohol, insoluble in ether. According to Löwe (Fr. 13, 121), it possesses the formula $C_{21}H_{18}O_9$, and gives a lead salt $3PbO, 2C_{21}H_{18}O_9$, but this most probably requires revision.

According to Etti (Annalen, 186, 332), catechutannic acid is an anhydride of catechin, and is derived from this substance by elimination of water. It is said to be produced when an aqueous solution of catechin is heated to 110° (Löwe, *ibid*. 12, 285), or by boiling catechin with solutions of the alkali carbonates. Again, catechin is decomposed at its melting-point with evolution of water and formation of a product resembling catechutannic acid, and aqueous solutions of catechin on long standing become brown-coloured with apparent formation of this compound. That the products obtained by these methods resemble catechutannic acid is certain, but the subject has not been fully investigated.

Catechutannic acid solution gives a precipitate with lead acetate, and also resembles catechin in giving a green colouration with ferric chloride, and the phloroglucinol reaction with pinewood and hydrochloric acid. It is a powerful tanning agent, and appears to differ but little from the so-called ' catechol ' tannins.

Three other catechin anhydrides have been described, viz. the *second* anhydride $C_{42}H_{34}O_{18}(?)$, (Etti), which is produced by heating catechutannin to 162° ; the *third* anhydride $C_{21}H_{16}O_7(?)$, formed by digesting catechin with boiling dilute sulphuric acid for several hours ; and the *fourth* anhydride, which is obtained by heating catechin with hydrochloric acid at 160°-180°. These compounds consist of reddish-brown powders, and the fourth substance is insoluble, both in alkaline solutions and all solvents. A product similar in properties to Etti's fourth anhydride is readily formed by adding sulphuric acid to a hot acetic acid solution of catechin (Perkin). A bright orange powder almost immediately separates, and this, on analysis, gave C=63·26 p.c. ; H= 3·89 p.c. It is interesting to note that the formation of these red anhydrides, or *phlobaphenes* is characteristic of all the catechol (phlobo) tannins.

According to Perkin and Yoshitake, gambier catechu contains a small quantity of a second catechin, which crystallises in small prisms, devoid of water of crystallisation, and melts at 235°-237°. Its general reactions are identical with those of ordinary catechin, and by fusion with alkali it also gives *phloroglucinol* and *protocatechuic* acid. The azobenzene compound $C_{15}H_{12}O_6(C_6H_5N_2)_2$, orange-red needles, melts at 215°-217°.

Finally, there are present in catechu, certain brown substances known as *rubinic* and *japonic* acids, which, according to some writers, appear

to have been formed by the oxidation of the catechin. Their chemical nature is, however, unknown.

Catechin, though largely employed for tanning purposes, does not precipitate a gelatine solution, and is not itself a tannin matter. On the other hand, it is absorbed by the hide, and there gradually passes into catechutannic acid.

Dyeing Properties.—On cotton, catechu is largely used for the production of the well-known 'catechu brown,' which is exceedingly fast to light, acid and alkaline solutions, and also to bleaching powder. To obtain this, cotton is steeped in a hot solution of catechu (1–2 p.c.) to which has been added about 6 p c. of copper sulphate, reckoned on the weight of the catechu employed. The material is allowed to remain in the bath as it cools, and without washing is then treated in a warm or boiling second bath containing 1 or 2 grams of bichromate of potash per litre. According to Hummel and Brown (J. Soc. Chem. Ind. 1896, 15, 422), in this operation the copper sulphate probably converts the catechin into catechutannic acid, and this is subsequently oxidised to japonic acid by the action of the bichromate. The colour is apparently intensified by the formation of a basic copper chromate Gambier catechu is also employed in dyeing compound shades with logwood, fustic, and alizarin in conjunction with bichrome, and with bismarck brown, magenta, &c. In the latter case catechu-tannin forms the mordant for the basic colour.

Wool may be dyed with catechu in a similar manner to cotton. In silk-dyeing, catechu is largely used for weighting purposes. The silk is steeped in basic ferrous sulphate solution, then in potassium ferrocyanide and hydrochloric acid, which causes the production of Prussian blue on the fibre. It is then worked in a strong solution of gambier to which stannous chloride solution has been added.

Bengal or Acacia catechu.—Bengal catechu is derived from the *Acacia catechu*, a tree 15 to 20 feet high, which is common in most parts of India and Burma To isolate the catechu which is present in the red heartwood, the tree is cut down while it is fullest of sap, and the internal portion is sawn into small sticks and extracted with boiling water. The liquid thus obtained is concentrated over a fire, and then allowed to evaporate spontaneously in shallow dishes. The extract thus obtained comes into the market as *Pegu* catechu, Brown cutch, and Brown catechu (Crookes, Dyeing and Calico Printing).

A purer substance, *kath*, or the pale catechu of India, is prepared by suspending twigs in the hot concentrated extract and collecting the crystals which thus separate.

Acacatechin $C_{15}H_{14}O_6,3H_2O$ can be obtained from the acacia kath by methods identical with those which are employed for the isolation of catechin from gambier catechu. It melts at 204°–205°, is somewhat more sparingly soluble in water than catechin, and when fused with alkali gives *phloroglucinol* and *protocatechuic acid.* The reactions of acacatechin and catechin, in so far as they have been observed, are identical, and there is no difference in the composition of their derivatives when prepared under similar conditions. On the other hand, the melting-points of the substances themselves,

and also of their derivatives, differ widely, as is evident from the following table (Perkin and Yoshitake) :—

	Acacatechin	Catechin
Pentaacetyl derivative	158°–160°	124°–125°
Pentabenzoyl ,,	181°–183°	151°–153°
Azobenzene ,,	198°–200°	193°–195°
Tetramethyl ,,	152°–154°	144°–146°
Acetyl ,,	135°–137°	92°–93°

It appears certain, therefore, that catechin and acacatechin are isomerides, and it is possible that the latter may, on the basis of v. Kostanecki and Lampe's formula for catechin, be represented thus (Perkin, private communication) :
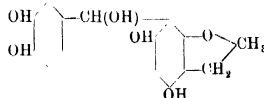
a point which should not be difficult to determine.

Bombay or Areca catechu. This variety is obtained from the fruit of the *Areca catechu*, or betel-nut palm, a tree which is common in tropical Asia. Though its chief constituent resembles catechutannic acid, catechin itself has not been isolated from this product. It possesses a bright-chocolate and sometimes an orange-brown colour, and yields, on dyeing, very similar results to the ordinary cutches.

Mangrove cutch. Mangrove cutch is obtained from the bark of the mangrove *Ceriops candolleana*, and is of somewhat recent employment. In its preparation it is preferable to extract the fresh bark, which is of a light colour internally, rather than the stored product which has become red, or is said to have 'sweated.' The extract, on evaporation, becomes deep-red in colour, and the object of the manufacturer is to prevent this anhydride formation from going too far, otherwise a certain portion of the extract is rendered insoluble in water.

By fusion with alkali, it gives *protocatechuic acid,* but at present no catechin has been isolated from it (Perkin, private communication). When dissolved in sodium bicarbonate solution, acetic ester extracts an almost colourless tannin, which possesses the properties of a catechol tannin.

For many purposes, mangrove cutch is competing closely with the other varieties of catechu, and this competition will no doubt become keener if its quality can be further improved.

Mahogany. According to Caseneuve (Ber. 8, 828), mahogany wood contains a catechin.

**Kino or Gum kino** (*see* under KINOS).

A. G. P.

CATELLAGIC ACID $C_{14}H_4O_6$. Schiff (Ber. 12, 2590), on heating protocatechuic acid with arsenic acid, obtained a substance which he named catellagic acid, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. Perkin and Nierenstein (Chem. Soc. Trans. 87, 1417) obtained apparently the same substance by the oxidation of protocatechuic acid, and also parahydroxybenzoic acid with potassium persulphate and sulphuric acid. According to the latter authors, catellagic acid crystallises from pyridine in colourless needles, which melt above 360°, and sublime with but moderate carbonisation at higher temperatures. Solutions of the alkali hydroxides dissolve it with a pale-yellow colour,

and with nitric acid it gives a magenta-coloured liquid. *Diacetylcatellagic acid,* colourless prismatic needles, melts at 322°–324°.

Catellagic acid, by distillation with zinc-dust, gives *fluorene,* and is closely related to ellagic acid. Its constitution (P. and N.) may be expressed as follows :—
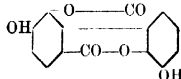
$$\text{OH} \underset{\underset{\displaystyle \text{OH}}{}}{\overset{\displaystyle O\text{——}CO}{\underset{\displaystyle CO\text{—}O\text{—}}{\big|}}}$$

From the oxidation products of parahydroxybenzoic acid, Perkin and Nierenstein isolated, in addition to catellagic acid, a second compound, $C_{14}H_8O_6$, colourless needles, m.p above 360°. This, which gives the diacetyl derivative $C_{14}H_6O_6(C_2H_3O)_2$, colourless needles, m.p. 267°–268°, and by distillation with zinc-dust fluorene, possesses the formula :

$$\text{OH} \underset{\underset{\displaystyle \text{OH}}{}}{\overset{\displaystyle O\text{—}CO}{\underset{\displaystyle \text{—COOH}}{\big|}}}$$
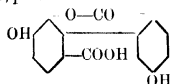
and evidently originates from the interaction of one molecule of protocatechuic acid and one of parahydroxybenzoic acid   A. G. P.

CATHARTIC ACID *v.* SENNA LEAVES.

CATHARTIN *v.* SENNA LEAVES.

CATHARTOGENIC ACID *v.* SENNA LEAVES.

CATHARTOMANNITE *v.* SENNA LEAVES.

CAULIFLOWER. A variety of *Brassica oleracea,* in which numerous imperfect flowers form a compact head, which forms the main edible portion.

An American analysis shows the edible portion to contain :

Water	Protein	Fat	Soluble carbohydrates	Ash
90·8	1·6	0·8	6·0	0·8

                            H 1.

CAULOPHYLLINE *v.* CYTISINE.

CÂY CÂY FAT or **COCHIN CHINA WAX** *v.* WAXES.

CAYENNE PEPPER *v.* RESINS.

CEANOTHUS WAX *v.* SNOWBRUSH WAX ; art. WAXES.

CEDAR CAMPHOR *v.* CAMPHORS.

CEDAR OIL *v.* OILS, ESSENTIAL.

CEDRA. (*Cedrat,* Fr.) The fruit of a species of orange, citron, or lemon. The peel is very thick, covered with an epidermis containing a fragrant essential oil, used for flavouring preserves, also used whole for wet comfits, and cut in quarters for dry comfits. A liqueur is made from it by gathering the fruit before it is ripe, and grating the peel into brandy.

CEDRELA TOONA. The *Cedrela toona,* the Toon or Indian mahogany tree, is a large tree 50–60 feet, although occasionally reaching 100 feet in height, the wood of which closely resembles mahogany and is imported into England under the name of ' Moulmein Cedar,' and much used for making furniture. It occurs in the tropical Himalaya from the Indus eastward, throughout the hilly districts of Central and Southern India to Burma, and is also found in Java and Australia. The flowers constitute one of the less important Indian natural dyestuffs, and are reputed to yield both a red and a yellow dye (known in Bengal as ' Cunari,' which is

applied without mordants). Although employed for dyeing purposes alone, the flowers are also used in Burma in conjunction with safflower and together with turmeric to produce the sulphur-yellow colour or ' basanti ' of Cawnpore.

To isolate the colouring matters, Perkin (Chem. Soc. Trans. 1912, 101, 1539) digested an aqueous extract of the flowers with a little hydrochloric acid at 70°–80°, which caused the separation of a reddish-brown precipitate. This collected and dried was exhausted with boiling alcohol, and the solution on evaporation deposited a small amount of a red microcrystalline powder. By re-crystallisation from pyridine and removal of an insoluble amorphous impurity, this separated in large orange-coloured leaflets which contained pyridine, and became red and opaque when washed with benzene or alcohol, the pyridine being thus eliminated.

It melted at 285°–287°, and with cold concentrated sulphuric acid gave a deep indigo blue liquid, resembling in this property bixin, the colouring matter of annatto, *Bixa orellana* (l.c.). This compound proved to be identical with the red colouring matter *nycanthin* isolated by Hill (*ibid.* 1907, 91, 1501) from the flowers of *Nycanthes arbor-tristis,* to which the erroneous m.p. 234°–235° has been assigned. The amount which is present in the Toon flowers is very small and does not seem to average more than 0·1 p.c. Though there appears to be little doubt that nycanthin and bixin are closely related, the connection between the two compounds cannot be predicted with any reasonable certainty until chemists are in agreement as to the correct formula of bixin. The analyses of Hill and of Perkin indicate that nycanthin contains approximately ($C = 72·68$, $H = 7·75$, and the simplest formula to which this corresponds is $C_{15}H_{18}O_2$. Among the numerous expressions proposed for bixin is, however, that of van Hasselt (cf. Annatto), $C_{29}H_{34}O_5$, and should this eventually prove to be correct, then nycanthin is possibly an oxy- or hydroxy-bixin, $C_{29}H_{34}O_6$ ($C = 72·8$; $H = 7·1$).

Addition of zinc-dust to the hot orange-yellow coloured alkaline solution of nycanthin causes decolorisation. From this by acidification a colourless or faintly yellow precipitate separates, and this, as is well known, is a property also possessed by bixin.

Cotton on immersion in a boiling dilute solution of nycanthin in sodium carbonate, and subsequently rinsing with acidified water, is dyed an orange shade indistinguishable from that given in these circumstances by annatto, a fact which again points to a relationship between the two colouring matters.

The flowers of the *Cedrela toona* contain in addition to nycanthin a fair amount of *quercetin* probably as glucoside, and also a second flavone or flavonol dyestuff, the identity of which was not ascertained. A sugar, $C_{12}H_{22}O_{11}$, is also present, and this after purification melted at 165°–168°.

Cotton and woollen fabrics can be dyed a dull yellow colour by mere immersion in a boiling extract of Toon flowers. This, however, is not permanent, and is removed, although much more quickly from cotton than wool, by the action of soap or dilute alkali. Better results are obtained by the employment of mordants, and

the following shades were obtained with mordanted woollen cloth :—

Chromium	Aluminium	Tin	Iron
Dull brownish-yellow.	Full golden-yellow.	Bright yellow. olive-brown.	Dull olive-brown.

During these operations, nycanthin or its glucoside apparently plays no part, and the colours obtained are due to the flavone glucosides present. Not only the flowers but the seeds of the *Cedrela toona* are stated to give a red dye
A. G. P.

CEDRIRET. A substance found in woodtar by Reichenbach and recognised by Liebermann as a quinone-like substance and termed by him *cærulignone*. Hofmann showed that it was tetramethoxydiphenyl quinone, formed by the oxidation of pyrogallol dimethyl ether (v. CŒRULIGNONE and QUINONES).

CELERY. *Apium graveolens.* The blanched stems are used for food.

The composition, as given by American analyses, is :

Water	Protein	Fat	Carbohydrates	Ash
94·4	1·4	0·1	3·0	1·1

A more detailed analysis is given by Church (Foods, 1889) :

Water	Protein	Starch and mucilage	Sugar	Cellulose	Ash
93·3	1·4	1·6	2·0	0·9	0·8

Mannitol is one of the chief carbohydrate constituents. Asparagine (about 0·5 p.c.) and tyrosine, are among the nitrogenous constituents (Bamberger and Landsiedl, Monatsh. 1904, 25, 1030).

The characteristic odour and flavour of celery are due to an essential oil, which, according to Ciamician and Silber (Ber. 29, 1799 ; 1897, 30, 492, 1419), consists of a terpene, probably $C_{15}H_{24}$, and two acid bodies, *sedanonic* acid $CO_2H·C_6H_8·CO·C_4H_9$ and *sedanolic acid*

$$CO_2H·C_6H_8·CH(OH)·C_4H_9$$
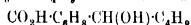
the anhydride $C_6H_8 \underset{CO-}{\overset{C(:C_4H_8}{<}} >O$ of the

former and the lactone $C_6H_8 \underset{CO---}{\overset{CH(C_4H_9)}{<}} >O$

of the latter appear to be the constituents upon which the smell of the celery depend. Palmitic acid and a phenolic substance are also present.
H. I.

CELERY OIL *v.* OILS, ESSENTIAL.

CELESTINE BLUE *v.* OXAZINE DYESTUFFS.

CELESTITE or **Celestine.** Native strontium sulphate ($SrSO_4$), forming orthorhombic crystals isomorphous with barytes ($BaSO_4$). The crystals are colourless or yellowish, but sometimes they show a pale tinge of sky-blue, and on this account the mineral receives its name. The mineral is often very like barytes in appearance, and it is also heavy (sp.gr. 3·9 ; of barytes, 4·5) ; it is most readily distinguished by the colour the powdered mineral moistened with hydrochloric acid imparts to the Bunsen flame. Numerous finely crystallised specimens have been found in the red marls of Triassic age in the neighbourhood of Bristol, and in the sulphur-mines near Girgenti in Sicily. Deposits of celestite occur in beds of Cretaceous age over a very wide area in Russian Turkestan ; and the mineral is found also in Baluchistan. The

largest crystals, measuring a foot across, are from a cave in limestone on Strontian Island, Lake Erie, Ohio. Workable deposits are mined in Arizona and California. The mineral is dug in numerous shallow pits in Gloucestershire and Somersetshire, the production amounting to about 20,000 tons per annum, valued at about 1l. per ton. Most of this was exported to Germany, where in the form of strontium hydroxide, it was used in the refining of beetsugar. It is also converted into strontium nitrate for making red fire in pyrotechny. For details respecting the British occurrences, *see* Special Reports on the Mineral Resources of Great Britain, vol. iii. (Mem. Geol. Survey), 1915, 2nd ed. 1918.
L. J. S.

CELLOIDIN. Trade name for a purified form of pyroxylin.

CELLOSE (CELLOBIOSE) *v.* CARBOHYDRATES.

CELLOTROPIN. Trade name for benzoic ester of arbutin.

CELLULASE *v.* ENZYMES.

CELLULOID (*Pyroxylin Plastic*) is a colloid composed of soluble nitrocellulose, approaching $C_{12}H_{16}(NO_2)_4O_{10}$ in composition, together with camphor. It is obtained by gelatinising nitrocellulose by means of a solution of camphor in ethyl alcohol or a similar menstruum. The word ' celluloid ' is a registered trade-mark in the United States. The substance was first produced by Alexander Parkes, of Birmingham, in England, under the name of ' Parkesine.' Parkes was succeeded by Daniel Spill, of Hackney, London, who adopted the name of ' Xylonite,' under which name it is still well known in Great Britain. Other trade names are Fiberoid, Py-ra-lin, Viscoloid, &c. Great improvements in the manufacture, especially in mechanical features, were made by John W. Hyatt, of Newark, N.J., U.S.A., and the material first became a commercial success in the United States.

The nitrocellulose employed is preferably made from tissue paper by subjecting it for 20 minutes or longer to the action of a bath of mixed sulphuric and nitric acids containing 19–20 p.c of water, at a temperature of 30° or more. The resulting nitrocellulose is thoroughly washed with water to free it from acids, and bleached. The surplus water is then removed.

The nitrocellulose is then mixed with alcohol, camphor, and if necessary, pigments and fillers, and thoroughly incorporated in a kneading machine. Transparent material receives a small percentage of urea as a stabilizer. The dough-like mass is worked and formed into sheets between slightly heated rolls. These sheets are consolidated in hydraulic presses heated to about 75°C. into a solid cake, from which after cooling sheets of the desired thickness are cut ; or the mass taken from the rolls is placed in a heated cylindrical hydraulic press, provided with suitable nozzles and dies, from which it emerges in the shape of tubes, rods, or the like, of any desired cross-section. Rods may also be made out of the solid cake previously mentioned, by forcing a cutting tool through it. All this material has to be freed from its excess of solvent, and is seasoned in rooms, heated to 30°, where it is kept for a period of days, weeks, or months, according to thickness. The camphor solvent

usually employed is denatured alcohol, owing to the fiscal policy of the countries concerned, but wood alcohol, pure grain alcohol, and a mixture of one or both of them with fusel oil, or its various constituents, have also been widely used. Owing to the great fluctuations in the price of camphor in recent years, the attempts to make this substance synthetically, and to find a substitute for it, have been pursued with vigour. Synthetic camphor in commercial quantities is an accomplished fact, and is the equivalent of the natural product The search for substitutes was begun in the early eighties ; the most suitable found so far being acid derivatives of aromatic amines.

Celluloid is coloured by means of mineral colours, lakes, and coal-tar dyes, to reproduce the appearance of some more expensive substances, such as ivory, tortoise-shell, leather, coral, amber, &c., or to replace glass in the manufacture of articles in which brittleness is a serious disadvantage. • A special variety of celluloid is used in the manufacture of cinematograph film. This contains a higher proportion of nitrocellulose than ordinary celluloid, and the nitrocellulose is more highly nitrated.

Celluloid, while highly inflammable, is non-explosive under any conditions to which it may be subjected in the work of cutting, turning, or moulding, or indeed under any normal conditions. Its specific gravity varies with its composition. It is about 1.35 for the unpigmented material.

Celluloid is plastic at a temperature of $75°$, and in practice it is usually softened in boiling water or on a steam table preparatory to moulding. This property of turning plastic at comparatively low temperatures, and its hardness and elasticity at ordinary temperatures, as well as its resistance to the action of water, dilute acids and many other agents, constitute its great technical value. It is used extensively in the manufacture of combs, and other toilet articles, knife handles, piano keys, collars, toys, and for a great variety of other purposes.

A relatively less important branch of the celluloid industry is concerned with the manufacture of artificial leather by spreading a solution of celluloid on fabric. Celluloid solutions are also used in the manufacture of patent leather, and for metal lacquers, wood enamels, incandescent mantle dips, and a variety of other purposes where a quick drying water-proof transparent or pigmented coating is required, which may be either hard or flexible.

For a method of analysing celluloid, see Hervé, Caoutchouc et Gutta Percha, 1918, 15, 9601 ; J. Soc. Chem. Ind. 1918, 686 A.

J. N. G.

CELLULOSE, considered physiologically, is the main product of vegetable life. It is the preponderating constituent of all vegetable tissues, and essential to the cell as the structural unit. For while the synthesising activity of the cell is identified with its protoplasmic contents, its main function is the building up of non-nitrogenous substances, of which cellulose is the chief ; elaboration of cellulose, in fact, is synonymous with growth. As an organic product it is known to us in the specialised and diversified forms of plant structures, which are employed in industries either in their original form or after treatment for separation of their fibrous components.

Cellulose is the basis of our staple textile and paper-making industries, and, when modified by various chemical treatments, of modern high explosives, 'celluloid' products and 'artificial silk.'

Cellulose, as a component of vegetable foodstuffs, and in connection with agriculture, is economically important, and is a dominant factor of the cycle of processes, organically interdependent, of the vegetable and animal worlds.

By cellulose, as a chemical individual, we understand usually the residue from the exhaustive alternate treatment of vegetable tissues with alkaline solvents and weak oxidants. Generally, no cellulose is isolated on the large scale except as the result of a chemical treatment, more or less drastic, of fibrous raw materials ; and all that we know of cellulose as a chemical individual results from the study of products so obtained. The typical cellulose is the substance of bleached cotton, the bleaching process such as above described removing the substances other than cellulose with which it is associated in the plant. So obtained, it is a white substance, translucent when viewed under the microscope, but more or less opaque in the mass. This appearance is a consequence of the peculiar form of the cotton fibre, a flat thin-walled tube, the fibrillæ of which are membranously disposed.

The following brief outline of the special chemistry of cellulose necessarily precedes an account of its industrial applications, so far as they involve chemical principles or processes of treatment.

CELLULOSE — Generally, the non-nitrogenous skeleton of plant structures. Type : the fibre substance of cotton, freed from associated ' impurities ' by processes of (1) alkaline hydrolysis and oxidation (bleaching) ; (2) digestion with hydrofluoric and hydrochloric acids, to remove mineral impurity or ash constituents.

Composition.—Elementary : C, 44.4 ; H, 6.2 ; O, 49.4 ; whence the empirical formula, $C_6H_{10}O_5$.

Constitution.- By solution in sulphuric acid as disulphuric ester $n \cdot [C'_6H_8O_2(SO_4H)_2]$ and ultimate hydrolysis, the colloidal aggregate is resolved with formation of dextrose in large proportion (Flechsig. Zeitsch. physiol. Chem. **7,** 523) The identity

$$[n \cdot C_6H_{10}O_5] + n \cdot H_2O = n.C_6H_{12}O_6$$
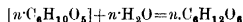
which has been assumed, has not been verified experimentally ; a maximum yield of 90-100 p.c. dextrose [theory, 111.11], but only indirectly estimated and accompanied by acid products, leaves the problem undetermined (Ost and Wilkening ; Chem. Zeit. 34, 461). *See* also recent critical discussions (Chem. Soc. **Trans.** 1918, M. Cunningham : Cross and Bevan). Cellulose is thus variously regarded :

1. As a polyhexose anhydride ; (a) aldose, (A. G. Green, Zeitsch. Farb. Chem. **3,** 97), (b) ketose (Fenton ; Cross and Bevan, Chem. Soc. Trans. 82, 361, 366).

2. As a polycyclohexane derivative ; this view is based on further considerations of density and molecular volume (Cross and Bevan, Ber. 1909, 42, 2198).

3. As an essentially labile aggregate, that is

of variable constitution or configuration, varying according to the action of reagents (Cross and Bevan, Chem. Soc. Trans. 85 ; Cellulose Researches, ii. 1905).

Cellulose and water.—Hydration. Constitutional water is retained by cellulose in the air-dry condition. Cotton holds 6–8 p.c., varying with temperature and moisture of atmosphere. Cotton which has been hydrated by treatment with alkalis (mercerisation) or solvents (*infra*) or by prolonged attrition in presence of water, shows an increased capacity for moisture when air-dry, and retains 9–11 p.c. Conversely, the action of condensing acids (HCl,HBr) produces modified aggregates (' hydrocellulose ') with a lower capacity (3–5 p.c.). Cellulose separated from its solutions, or regenerated from its derivatives by the action of reagents, shows a maximum hydration capacity ; the colloidal or gelatinous hydrates having the composition (in contact with water at ordinary temperatures) :

Cellulose	20–10 p.c.
Wat r	80–90 ,,

Cellulose and solvents.—Insoluble in all neutral solvent liquids, cellulose is dissolved by :

1. Concentrated solutions of zinc chloride (40–50 p c. $ZnCl_2$), on heating at 80°–100° ; when previously hydrated, at lower temperatures.

2. Solution of zinc chloride in twice its weight of HCl·Aq (35 p c HCl) · this reagent rapidly attacks and resolves the aggregate. Aqueous hydrochloric acid of maximum concentration ($>$40 p c. HCl) acts similarly (Wilstatter, Berl. Ber. 46 (1912) 240) but with fixation of negative groups (Cl) in stable union with the products (M. Cunningham, Trans. Chem. Soc *l.c.*).

3. Solutions of cuprammonium hydrate containing :

Cu, as $CuO \cdot nH_2O$.	. . 2·5–3·5 p.c.
NH_3 (as NH_4OH)	. . 15 p c

Ethylene-diamino-cupric solutions act more powerfully (W. Traube, Berl. Ber. 44, 3319 (1911)).

From solutions 1 and 3, the cellulose may be recovered quantitatively, but as a hydrate and otherwise modified in constitution.

4. Concentrated solutions of certain metallic sulphocyanides at high temperatures, 120°–140°.

Reactions.—The above reactions resulting in solution of the cellulose are characteristic ; otherwise it is exceptionally non-reactive. By dilute solutions of iodine, in presence of certain dehydrating agents, it is coloured blue

Cellulose compounds. A. **Synthetical derivatives. Esters.**

(*a*) *Nitrates.* By direct reaction with nitric acid, usually in presence of sulphuric acid, in which case unstable mixed esters are formed as a stage in the reaction, the NO_3 displacing the SO_4H residues (Cross, Bevan and Jenks, Berl. Ber. 34 (1902) 3496). The esters are formed without sensible structural modifications. They are purified from residual SO_4H by prolonged boiling with water, and are then ' stable.' A series of these esters is known, the highest approximating to the trinitrate (C_6) (gun-cotton); the intermediate terms—dinitrate—being soluble in ether-alcohol (collodion cotton), the lowest having physical properties but little different from the original cellulose.

These esters are variously formulated as

nitrates of a reactive unit of $C_6 - C_{12} - C_{24}$ dimensions.

Solvents.—The special solvents of these esters are acetone, ether-alcohol, nitrobenzene.

A diversified range of solvents is enumerated in a paper by H. de Mosenthal (J. Soc. Chem. Ind. 1907).

Saponification.—By certain alkaline and reducing agents (alkaline sulphydrates) the nitric groups are eliminated and cellulose regenerated.

(*b*) *Acetates.* By reaction with acetic anhydride under various conditions : (1) at 110° : direct formation of monoacetate (C_6) insoluble in all neutral solvents and in the solvents of cellulose. (2) At 140°–160° : formation of higher acetates, attended by solution in the reaction mixture. (3) In presence of catalytic agents ($ZnCl_2 - H_2SO_4 - H_3PO_4$) : at intermediate temperatures ; H_2SO_4 determines reaction at 25°–30°. The extreme products are mixtures of tri- and higher acetates. (4) When the reaction mixtures are diluted with hydrocarbon, the fibrous cellulose may be acetylated without solution or visible structural change.

Industrially important acetates are the acetone soluble esters $C_{12}H_{16}O_8 \cdot OAc_5$ produced by acetylation with mixtures of Ac_2O and H_2SO_4. These are the basis of aeroplane varnish-dopes. *Solvents* of the higher acetates, are chloroform, acetone, phenol.

For an exhaustive account of the industrially important types, see E C. Worden, J. Soc. Chem, Ind. 1919.

Saponification.—The acetyl groups may be removed by boiling with alkaline solutions, the cellulose being regenerated. In quantitative determinations the saponification may be effected by boiling with normal sodium hydroxide diluted with an equal volume of alcohol.

(*c*) *Formates.*—Cellulose and formic acid interact at 60°–100° ; in presence of catalysts the reaction proceeds to complete solution. The limit of esterification appears to be the diformate (C_6), but the product is unstable, decomposing spontaneously with liberation of formic acid (1 mol.). The reactions are not those of simple ester (anhydride) formation ; the celluloses in reaction appear to undergo constitutional change (Cross and Bevan, J. Chem. Soc. Ind. 1911, 99, 1450 ; Berl and Smith, Berl. Ber. 1907, 40, 906 ; Woodbridge, J. Amer. Chem. Soc. 1909, 31, 1067 ; Dewing, *ibid.* 1911, 33, 1179).

(*d*) *Acid-sulphuric esters.* By the action of sulphuric acid an extended series of esters is formed, which have been described as cellulose sulphuric acids. But they are certainly derivatives of products of resolution. The first stage results in the formation of a disulphuric ester $C_6H_8O_3(SO_4H)_2$, but its relationship to the parent complex is doubtful. The ester is soluble in water ; the Ca, Ba, and Pb salts are insoluble in alcohol. By progressive hydrolysis the cellulose is ultimately resolved in the direction of dextrose (*see* M. Cunningham and Cross and Bevan, *l.c.*).

(*e*) *Aceto-sulphates and mixed esters*, containing the SO_4H residues associated with acetyl and other negative groups in combination, are obtained when sulphuric acid is allowed to act under regulated conditions simultaneously with other esterifying agents. Thus a mixture of acetic anhydride (50 parts), glacial acetic acid

(50 parts), and sulphuric acid (4–6 parts), acts rapidly at 30°–40°. The first product appears to be a neutral body of the empirical formula

$$(4C_6H_7O)SO_4(C_2H_3O_2)_{10}$$
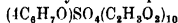
and under the action of water to undergo an internal hydrolysis, the SO_4 group becoming SO_4H, which forms a stable combination with bases. The Mg, Ca, Zn salts are insoluble in water, but soluble in acetone.

(*f*) *Benzoates* result from the action of benzoyl chloride in presence of alkaline hydroxides. A monobenzoate (C_6) is obtained by treating cellulose with a solution of sodium hydroxide of 10 p.c. (NaOH) strength, and shaking with benzoyl chloride. This benzoate is formed with only slight structural change. The dibenzoate (C_6) is obtained by the interaction of benzoyl chloride and alkali cellulose (mercerised cotton) in presence of sodium hydroxide solution (15 p.c. NaOH). Its formation is attended by structural change; the fibrous cellulose is disintegrated, the dibenzoate being an amorphous substance. The dibenzoate is soluble in acetic acid and chloroform.

Mixed esters, containing the benzoyl and nitric residues, result from the action of nitric acid upon the benzoates. Simultaneously a nitro- group enters the benzoyl residue.

Alkali cellulose. The fibrous cellulose undergoes considerable structural modification under the action of solutions of sodium hydroxide of 12–15 p.c. NaOH. These reactions and phenomena were first studied by Mercer. They are the basis of the process of *mercerisation* (*q.v.*) under which cotton-yarn and cloth assume a special lustre and silky finish. There is a definite synthetical reaction in the ratio $C_6H_{10}O_5 : 2NaOH$, which is a stage in the formation of the dibenzoate (*supra*).

The compound is completely dissociated by water; by treatment with alcohol an equilibrium is reached when the reagents are associated in the ratio $C_{12}H_{20}O_{10} : NaOH$.

The alkali-cellulose hydrate, of composition :

Cellulose . .	30	cellulose : sodium hydrate
Sodium hydrate	15	$C_6H_{10}O_5$　　2NaOH
Water . .	55	

is the first stage in the synthesis of

Cellulose xanthogenic acid, which results from the interaction of the alkali cellulose and carbon disulphide at ordinary temperatures. The sodium salt is soluble in water. It is an unstable compound, the solution undergoing spontaneous progressive change. The solution, which is highly colloidal, finally solidifies. By means of the characteristic reaction of the xanthates with iodine

$$CS{<}{{OX\ XO}\atop{SNaNaS}}{>}CS + I_2$$

$$= 2NaI + CS{<}{{OX{-}XO}\atop{S{-}{-}S}}{>}CS$$
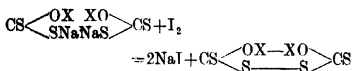
the progress of the change may be followed, the essential feature being the elimination of the CS_2 residues with reaggregation of the cellulose units. Well-marked stages in the series occur at the points denoted by the empirical formulæ $C_{12}H_{19}O_9$CSSNa, $C_{24}H_{39}O_{19}$·CSSNa. The former represents an equilibrium attained after the solution has remained for some hours at the ordinary temperature ; the latter is reached in

from three to four days. The cellulose under the reaction acquires a more acid character, an additional OH group combining with alkali. The lower terms of the series, *e.g.* $C_{48}H_{78}O_{39}$. CSSNA, though insoluble in water or dilute saline solutions, are dissolved by the addition of sodium hydroxide. The sodium atom in combination with the CSS residue is not attacked by weak acids such as acetic acid. By double decomposition with soluble salts of Cu, Zn, &c., the corresponding xanthates are produced as insoluble colloidal precipitates.

In the above reactions the cellulose aggregate is maintained ; the solutions of the derivatives are viscous and colloidal ; but in the following

B. **Reactions of decomposition**, which are determined by hydrolytic and oxidising agents, the directions of resolution are extremely various, and the relationships of the products to the original aggregate are undetermined.

(*a*) *Sulphuric acid* dissolves the cellulose as a disulphuric ester , but decomposition attends the reaction, and on diluting and boiling, the hydrolysis is carried to the extreme molecular limit, the final product being dextrose (*supra*) ; but the reactions are not simple as generally stated ; they are complicated by relatively stable union of the SO_4H with the resolved cellulose ' residues,' and by tendency to reversion or condensation.

(*b*) *Hydrobromic acid* in ethereal solution attacks the cellulose profoundly with production of brom-methyl furfural. The formation of this compound indicates a previous or intermediate stage in which the products of resolution are molecular ketonic bodies of carbohydrate constitution (Fenton, Chem. Soc. Trans. 1901, 361).

(*c*) *Hydrochloric acid*, in presence of water, dilute sulphuric acid, and acids generally, attacks the cellulose aggregate with production of a variety of derivatives. (1) *Insoluble :* these are generally termed ' hydrocelluloses.' They are disintegrated residues of the original fibres ; they differ chemically from the parent aggregate in the presence of free aldehydic groups, and in readily yielding to the action of alkalis. (2) *Soluble* molecular products, chiefly dextrines and dextrose.

(*d*) *Alkaline hydroxides* and *alkalis* generally in the form of dilute solutions have little apparent action on cellulose—even when treated at elevated temperatures. Sodium hydroxide in solutions of concentrations of 12 p.c. NaOH and upwards, combines with the cellulose, producing profound structural modifications (mercerisation), but without resolving the aggregate.

At higher concentration and temperature the cellulose is partially dissolved ; but even under the conditions of a ' fusion ' at 180° the resolution is limited to the conversion into alkali soluble modifications, which are precipitated in the colloidal form on diluting and acidifying. At higher temperatures (250°) and with larger proportions of the alkaline hydroxides, the cellulose is resolved into acid products of low molecular weight, chiefly acetic acid and oxalic acid.

(*e*) *Oxidants.* The directions of oxidation of cellulose are likewise extremely diversified. The aggregate manifests considerable resistance to alkaline oxidants in dilute form, *e.g.* solutions of the *hypochlorites, permanganates* ; but when the limit is passed the oxidations which result

are drastic in the sense that the soluble products are of low molecular weight, chiefly carbonic and oxalic acids. The insoluble fibrous residues, more or less disintegrated, are known as *oxycelluloses*. They contain free aldehydic groups, are easily attacked by hydrolysing agents, and on boiling with hydrochloric acid (1·06 sp.gr.) are decomposed with production of some furfural.

Resolved by the action of *concentrated* solutions of the *hypochlorites*, cellulose yields chloroform and carbon tetrachlorides. The hypobromites give the corresponding bromine derivatives. Nitric acid (1·25 sp.gr.) at 80°–100°, converts cellulose into a series of ' oxycelluloses,' which are resolved on boiling with calcium hydroxide into acid products, among which isosaccharinic and dioxybutyric acids have been identified. In the original oxidation small quantities of the higher dibasic acids— saccharic and tartaric acids—are produced, but the main products are oxalic and carbonic acids.

· With *chromic acid* an endless series of oxidations may be effected, the degree of action depending upon the proportion of the active oxidant and the associated hydrolytic action of mineral acids. The oxycelluloses produced are distinguished by relatively large yields of furfural when decomposed by boiling HClAq (1 06 sp gr.). In presence of sulphuric acid there ensues complete combustion, and the reaction is the basis of quantitative analytical methods.

(*f*) *Resolution by ferment actions* Under the actions of specific organisms the cellulose complex is totally resolved, the main products being methane, hydrogen, and carbonic and fatty acids. The decomposition may be associated with the action of an enzyme ; but a remarkable feature of the process is the absence of intermediate products, at least in the cases hitherto investigated. In the digestive tract of the herbivora, cellulose is resolved, and from the investigation of the process, necessarily by indirect observations, it appears that, in addition to a destructive resolution to ultimate gaseous products, there occurs a resolution to proximate groups of high nutritive value, which are assimilated by the animal organism.

(*q*) *Resolution by heat* : *destructive distillation*. Cellulose heated at 100°–120° is dehydrated : at 150° decomposition is evidenced by change of colour. At this early phase maltol appears to be formed. The decompositions of cellulose at temperatures exceeding 250° are necessarily extremely complex.

The groups of products show an average proportion :

Solid 30 p.c.	Liquid 50 p.c.	Gaseous 20 p.c.
Charcoal or pseudo-car-bon	Containing acetic acid(2 p.c.),methyl alcohol (7 p.c.), acetone, furfural (12 p.c.)	Chiefly CO and CO_2

the actual proportions and composition of these mixtures varying with the temperature and duration of their heating.

By ' dry ' distillation *in vacuo* of cellulose (and starch) large yields of lævoglucosan are obtained. Pictet and Sarasin, Compt. Rend. 166 (1918) 28.

General view of the decompositions of cellulose. It is clear that the cellulose complex breaks down under destructive influences, in directions depending upon the nature of the attacking agent, its concentration, and all the surrounding physical conditions. The study of these decompositions has thrown but little light on the actual nature and constitution of the cellulose aggregate ; for the reason, perhaps, that we have endeavoured to maintain a basis of interpretation such as is applicable to ordinary molecular compounds or complexes. Cellulose is a typical amphoteric colloid . its reactions with hydrolytic reagents suggest many points of analogy with the state of a complex salt in solution (in water). Its component groups of unknown, but possibly small dimensions, appear to exist under a certain internal stress which determines migrations of H and OH under reaction. While, therefore, we have reduced the reactions of cellulose to a short systematic expression, it is clear that the main aspect of the subject cannot effectually be so treated, because it involves as theoretical basis the actual state of matter and the dimensions and distribution of the reactive unit-groups in the cellulose complex ; and this basis is, as yet, largely undetermined (*see* Cross and Bevan, Cellulose Researches, 1905, 1910).

The cellulose group. From the typical cellulose we pass to the diversified group of celluloses. Their general characteristics are those of the prototype ; the variations they present are especially such as involve the undetermined factors of constitution. With these there are certain correlative variations which afford an empirical basis of classification. These are (*a*) the degree of resistance to hydrolytic and to oxidising agents ; (*b*) the percentage yield of furfural when decomposed by boiling HClAq ; (*c*) elementary composition, in respect of the ratio C : O.

The fibrous celluloses are grouped as follows :

Type.	Cotton cellulose sub-group A. Bleached cotton.	Wood cellulose sub-group B. Jute cellulose.	Cereal cellulose sub-group C. Straw cellulose.
Hygroscopic moisture	·		
Elementary composition C : O	6-8 p.c.	9-11 p.c.	9-12 p.c.
	{ 44·0–44·4	43·0–43·5	43·5–44·5
	50·0	51·0	52-50
Furfural	0·1–0·4	3·0–6·0	12·0–15·0
Other characteristics	No active CO groups	Some free CO groups	Variable reactivity of *CO groups.

See Esparto Cellulose and the Problem of Constitution : Cross and Bevan, Chem. Soc. Trans. 113 (1918) 182.

Of these groups the following points may be noted :—

A. Comprises, in addition to cotton, other industrially important celluloses, *e.g.* flax, hemp, and rhea. They occur in the plant-world in association with compounds easily removed by the action of alkalis. They pass through the

cycle of reactions involved in their solution as xanthates, without hydrolysis to soluble derivatives.

B. These celluloses are obtained as products of decomposition of a compound cellulose. They may be regarded as partially hydrated or hydrolysed. They are more readily attacked by hydrolysing agents and, in the xanthate reactions, are partially resolved to alkali-soluble derivatives.

C. These celluloses are in most cases a complex of structural elements, and not homogeneous chemically. They are still less resistant than the preceding group, and more especially the furfural-yielding components, which are selectively attacked under certain conditions

The cellulose groups, as above, pass by imperceptible gradations into a heterogeneous class of natural products, which, while possessing some of the characteristics of the celluloses proper, are so readily resolved by hydrolytic treatment that they must represent a very different constitutional type or types. To this group of complex carbohydrates the class-name *hemicellulose* has been assigned They are structurally different from the fibrous celluloses, occurring mostly in the cellular form (parenchyma, &c.). They differ in physiological function, and in being readily resolved by hydrolysis into the crystalline monoses.

The foregoing *exposé* will enable us to group the *industrial and manufacturing applications of cellulose* in reference to first principles as follows :—

GENERAL.—The uses of the fibrous celluloses, more particularly of cotton and the cotton group, in which we may include flax, hemp, and ramie, depend, apart from the primary condition of length of ultimate fibre, upon the extreme chemical resistance of the fibre substance, which is a function both of the constitution of the ultimate groups and of their mode of union to constitute the aggregate itself.

Insensitiveness to oxidation is an obvious condition of such stability as is required for textile fabrics and paper, and, as evidence of resistance to atmospheric oxygen, we have the fact that flax and cotton fabrics and papers composed of these fibres have been handed down to us from antiquity, with little change. Next in order of importance is resistance to water and alkaline hydrolysis. This resistance enables textile fabrics to withstand periodical cleansing or laundrying, in which alkalis are the principal agents. In the purifying of textile fabrics by the bleaching processes and the preparation of paper pulps, the same negative qualities are of first importance.

Textiles are subjected to severe processes of alkali treatment, and to the action of bleaching agents, such as hypochlorites, without evident chemical or structural modification.

On the other hand, there is a limit of the resistance to oxidation, and any undue action of the ordinary bleaching agents leads to the formation of 'oxycellulose,' and structural weakening as an attendant result.

While extremely resistant to alkalis, the celluloses are sensitive to acids, and here again in bleaching, finishing, and dyeing processes, the incidental acid treatments require careful adaptation to the limit of sensitiveness of the cellulose.

SPECIAL.—*Constitutional moisture and hydration effects.* These involve a range of phenomena of obvious industrial importance. The normal moisture of cellulose has to be taken into account in the finishing of textiles, and their package for shipment. The condition of the fibres as regards hydration, of which the capacity for combining with atmospheric moisture is an index, directly affects the finishing processes which are chiefly the mechanical operations of mangling, calendering, and beetling.

The further *hydration* of the celluloses which takes place in the beating operations of the papermaker is of considerable practical importance, and affect the quality and character of the papers in a very great degree.

Cellulose and ash constituents. The normal ash of the cellulose of the cotton group is small in proportion, and we are not able to affirm that these inorganic constituents have any determining relationship to the constitution of celluloses, though this is an accepted probability.

It is a problem for colloidal chemistry to establish this relationship in specific terms. Industrially, the question arises only with regard to the aggregate.

Thus in the purest form of cellulose required as filter paper for the quantitative separations by chemists, it is of importance that the ash components should be reduced to a minimum.

This minimum of 0·05 p.c. by weight, is attained by digesting the cellulose with hydrofluoric acid and hydrochloric acid, and thoroughly washing the paper in pure water.

Pure unsized cellulose paper thus treated constitutes the well-known 'Swedish' paper, so called from its country of origin, but now produced in this country and other centres.

Cellulose as a typical colloid enters into characteristic combinations with inorganic oxides, and this property is an important basis of the processes of the dyer and printer.

Oxides of the polyvalent metals, notably of aluminium, chromium, iron, tin, and lead, are taken up by the celluloses from solutions of their salts, and the cellulose thus *mordanted* has increased special affinities for colouring matters.

A more special industrial application of this property is the method for making the mantle, now in common use for intensifying coal-gas illumination (Auer-Welsbach). The colloidal oxides of thorium and cerium in suitable proportions are fixed upon cellulose fabrics, which are then dried and ignited. The result is an inorganic skeleton of the original fabric, prepared in any desired form, and composed of the oxides in question.

The particular form fulfils the conditions of maximum illuminating surface, together with the desired degree of mechanical resistance to stand shock and wear and tear under the particular conditions of employment.

Cellulose and solvents. It is in the solutions of cellulose or its derivatives that the particular properties of the cellulose aggregate are evident.

In the case of the aqueous solvents observation shows that the cellulose, employed as fibre, passes through phases of progressive hydration with considerable distension until the final stage of homogeneous structureless solution is reached.

The general character of the solutions is their high viscosity, which imposes a limit of from 7 to 9 p.c. cellulose for solutions which require filtering.

The technical applications of these solutions depend upon the fact that the cellulose is brought into the plastic homogeneous structureless condition, in which it may be formed or shaped at will, and in finally reverting to the solid state preserves its structural continuity through the successive phases of dehydration.

The solution in zinc chloride has been used for making threads to be carbonised for electric incandescence lamps.

The solution is forced through narrow orifices into alcohol, which precipitates the cellulose as a transparent hydrated solid, retaining zinc oxide (hydrate) in combination. The solid hydrate is formed and manipulated in continuous length, and, when freed from zinc oxide and dried, is a structureless cylinder of cellulose. Heated out of contact with air, it is converted into a ' pseudo-carbon,' which constitutes the filament in question.

The solution of zinc chloride in hydrochloric acid has been employed for converting cellulose papers into a special agglomerated product or board, which is used as an insulating material and for structural purposes. The sheets or webs of paper are treated with the solvent by immersion, and the material thus attacked is then welded into the composite fabric by means of the adhesion of the viscous cellulose solution resulting from the attack.

The composite sheets or webs so produced are finally compacted by pressure, and then exhaustively washed to remove the solvents.

Cuprammonium. There are various industrial applications of this characteristic solvent. Textile materials are treated by passing through the solution. The cellulose is attacked superficially, and under the pressure of rolls the gelatinised product is distributed uniformly : the fabric is then dried. The fabric is thus coated with a varnish composed of cellulose and the hydrated copper oxide, of greenish colour which renders the fabric impervious to water and rot-proof.

Papers are similarly treated ; the sheets or webs being welded together under pressure. These fabrics have been known for a number of years as the ' Willesden ' waterproof fabrics.

The most important industrial application of the solution is in the manufacture of artificial cellulose threads, which are produced in various grades of fineness, and known as ' Artificial Silk,' ' Monofil ' (Lustra Cellulose, Soie Artificielle, Glanzstoff, Crin).

The process in its simplest form consists of the production of the solution by treating bleached cotton with the cuprammonium solvent, and filtering through fine metal-wire cloth to remove incidental impurities.

The solution is projected through orifices of varying diameter, according to the size of the threads to be produced, into solutions which precipitate or coagulate the cellulose.

The setting solutions are of two types, acid and alkaline.

The cellulose is precipitated as a hydrated solid, in continuous length, and is drawn forward at speeds varying from 20 to 50 metres per

minute, according to the diameter of the thread and the conditions of the precipitation.

In the case of fine filaments, constituting artificial silk, several of the threads so produced are twisted together to form a compound filament or yarn suitable for weaving purposes. The products are dried under special conditions, to secure maximum lustre and elasticity.

Cellulose esters. The application of the nitrates to high explosives is an application of cellulose that stands apart and depends, of course, upon the fundamental chemistry of the product.

The ratio of oxygen is such that the products contain the elements for their complete conversion into gaseous products when raised to the reactive temperature.

The nitrates in the fibrous form in which they are produced, are explosives of the disruptive or blasting type, and were exclusively so used for many years

The type of explosion required for the propulsion of projectiles, is a restrained or graduated combustion, which is determined by a change of form of the nitrates. These are convertible into plastic modifications under the action of their specific solvents, and in this state they may be formed or fashioned into threads, cylinders, or solids of any desired form or dimension. The combustion of these structureless solids, in its aggregate explosive effect, may be made to fulfil any desired ballistic conditions.

The most interesting case is that of the employment of nitroglycerine, itself a high explosive, and the basis of dynamite, to reduce the cellulose nitrate, acting as a solvent, to the structureless condition.

Mixtures of nitrocellulose and nitroglycerine, in suitable proportions, are drawn to threads and constitute with certain admixtures the modern explosives cordite, ballistite,&c. (*see* EXPLOSIVES).

The cellulose nitrates, treated with neutral solvents and subjected to a process of milling, are reduced to a structureless plastic mass. This may be reformed into solid substances which may be produced in any desired form or dimension. In sheets or film they constitute the basis or transparent carrier of photographic emulsions.

In solid form they are known as celluloid, xylonite, &c , and find endless applications both useful and ornamental (*v.* CELLULOID).

The solutions of nitrates in neutral solvents, such as ether-alcohol (collodion) or amylacetate, are used as varnishes and lacquers for various purposes.

The cellulose nitrates in ether-alcohol solution are employed industrially in the manufacture of artificial silk.

This, in fact, was the pioneer invention ' of Chardonnet,' and dates from 1883. The process of spinning consists in forcing the solution through capillary glass jets, either into air (Chardonnet) or into water (Lehner).

The thread is thus formed and obtained as a nitrate, in which form it is twisted into compound textile filaments, which are reeled into skeins of yarn.

A process of saponification for removing the nitric groups follows. This consists in digesting the nitrate yarn in solutions of ammonium-magnesium sulphydrates at ordinary temperatures.

As a result of the cycle of operations, the denitrated cellulose is obtained and constitutes the artificial silk of commerce.

The xanthogenic esters of cellulose in aqueous solution (viscose) are the basis of the production of artificial textile fibres, and the viscose artificial silk has displaced the pioneer product as well as to a great extent the cuprammonium product (Glanzstoff). The manufacturing process comprises the following operations :—

(1) Wood cellulose is converted into alkalicellulose (hydrate).

(2) After ageing, the product is treated with carbon disulphide in closed vessels.

(3) The xanthate is dissolved and filtered, and after ageing is projected through fine apertures into acid solutions, which cause rapid decomposition and reversion to ' cellulose.'

(4) The reprecipitated cellulose hydrate is dried and dehydrated under strain.

For a full description, see L. P. Wilson, J. Soc Chem. Ind. 1917, 817.

Cellulose acetates are the analogues of the nitrates with the radical distinction of being non-explosive, and, in fact, eminently stable compounds.

By treatment with their special solvents, they are dissolved to homogeneous viscous solutions, and they may be fashioned into films and solids as are the nitrates.

So far the industrial applications of the acetates have been limited chiefly by the prohibitive costs of production.

One important application, however, produces results so very much sui generis and in an arena where costs of production are a minor consideration, that it has led to extensive developments of the manufacture. Solutions of the acetate (6–8 p.c.) in ' organic ' solvent liquids constitute a viscous varnish-dope, which when applied to a (stretched) fine textile, cotton or flax cloth, produces a considerable shrinkage, and this under strain, as on the wing planes of the aeroplane, gives a taut, smooth surface, at the same time waterproofing the fabric and thus fulfilling the exacting technical specification of the effect required for these special and highly specialised structures.

The acetate is also used as a varnish covering of fine wire used in electrical construction. The acetate is a high insulator with exceptionally low inductive capacity.

Cellulose acetate has already been spun to artificial silk and coarser textile threads, but there has been so far no industrial development of the processes.

The technical interest of such a product is that it is employable as an ester, whereas the nitrate is entirely unsuitable, as such, for textile applications.

Cellulose and alkalis (Mercerisation). The action of alkaline hydroxide in strong solution (15–20 p.c. NaOH) upon cotton textiles, is the basis of a special industry. By converting the cotton fibre into the modified form, cotton yarns and fabrics are changed in appearance and acquire a silky lustre and touch.

The goods to be ' mercerised ' are passed through a solution of caustic soda in the cold. This produces the effect of considerable shrinkage accompanying the change of form and

dimensions of the ultimate fibre, from a flat membranous, to a thick-walled cylindrical homogeneous tube.

This shrinkage is resisted by placing the goods under the condition of mechanical strain, either during the process of alkaline treatment, or, after allowing the shrinkage to take place, the goods may be afterwards stretched to their original length.

The fundamental observations which condition this process were made by J. Mercer (1850–1860), but they remained undeveloped until late in the century (1880–1890).

The industry is now a considerable one, and is to a certain extent independent of fashion (see MERCERISING).

Cellulose and sulphuric acid. Whereas cellulose reacts with the more concentrated acids $(H_2SO_4 - H_2SO_4.H_2O)$ to form sulphuric esters, the acids of 67 0 to 78·0 p.c. H_2SO_4 (approximately $H_2SO_4.2H_2O - H_2SO_4.3H_2O$)hydrate, and dissolve the cellulose to a colloidal solution, from which, if immediately diluted, the cellulose is precipitated as a gelatinous hydrate (' Amyloid '). These reactions are industrially applied in the preparation of ' parchment paper,' or ' vegetable parchment.' A pure cellulose paper is passed through a bath of acid, and immediately, in continuous length, into water, which arrests the action of the acid and reprecipitates the cellulose superficially dissolved as a structureless colloid. After washing from the last traces of acid, the web of now parchmentised paper is dried under special conditions of strain to control the shrinkage of width (10–13 p.c.), so as to maintain an even surface and prevent deformation. To overcome the brittleness of the product, which would result from total drying, it is treated with solutions of neutral hygroscopic substances, such as glycerol or glucose, before passing on to the drying cylinders. A sufficient proportion is retained in the finished product to ensure a normal ' humidity.'

The total hydrolysis of cellulose to fermentable ' sugars ' is effected by dissolving in the more or less concentrated acid, and, after allowing the acid to act until the solution becomes limpid, diluting and heating the dilute solution. The acid is neutralised with chalk, filtered from the insoluble calcium sulphate, and concentrated. The industrial value of this process is obviously limited by the relatively low values of starches and the more economic conversion of these by simpler means and to superior products.

The compound celluloses (Vegetable fibres). While the simplest form of vegetable life is the cell, and the cell is, moreover, the universal originating unit, we observe, as we ascend the scale of plant organisation, an increasing variety of differentiations of this simplest structural unit graduating into the fibres and vessels of the stems of the higher flowering plants. It is to the presence of such elongated cells as warrant the designation ' fibre ' that these stems mainly owe their powers of bearing strains and resisting fracture. The uses to which these fibres are put in the arts depend upon the same characteristics of form, and obviously also on the nature of the fibre substance. So too the anatomy of fibrous stems is necessarily a main factor of the processes by which they are treated for the isolation of the fibres. We must

here except from the general anatomical view we are about to take the most important of the vegetable fibres, viz. cotton, which as a seed hair is distinct physiologically, and differs structurally from all other fibres employed for textile purposes.

The ' ultimate ' fibre is a hollow tube, the walls being thin and membranous ; it is attached at one end to the testa of the seed, the other being free, and there is no adhesion of the fibres to one another. The preparation of the textile fibre involves, therefore, only a mechanical treatment, and that of the simplest kind, for separating it from the seeds. The other vegetable fibres employed in the arts are without exception constituents of complex structures (stems and leaves) which require a more elaborate mechanical operation for their separation, in addition in many cases to a preparatory chemical treatment.

The fibres of stems are arranged according to the two main structural types of growth, the exogenous and endogenous In the exogenous stem of annuals (dicotyledonous) they constitute a localised tissue, the bast, which is an annular ring external to the wood and beneath the cortex. In the endogenous stem the fibres proper (bast fibres) are generally aggregated together with vessels into bundles known as fibrovascular bundles, which are scattered more or less irregularly throughout the cellular matrix.

In regard to the leaf, the two great divisions of the phanerogams are also contrasted ; the fibro-vascular bundles of the former are not only irregularly disposed, but interlaced (reticulate venation), whereas the leaves of the typical monocotyledon are characterised by a parallel arrangement of the bundles, and fulfil, therefore, a necessary condition of separation for textile purposes. Fibres of this class are amongst the most useful that we have. There is a distinction to be noticed, though rather of a technical than anatomical nature, between the vegetable fibres and ' fibrous substances ' . By the former we understand isolated bast fibres or fibro-vascular bundles, such as can be *spun* into a continuous length or yarn. A fibrous substance is any vegetable structure containing fibres. Many of these do not admit of being economically treated for the isolation of a textile fibre, but, on the other hand, are resolved by suitable *chemical* treatment into a fibrous mass or *pulp*, available for paper making. Many of our most valuable raw materials for this industry are of this nature. We may further distinguish, according to the above classification, (1) exogenous bast tissues, such as those of the Adansonia and Broussonetia (paper mulberry) and entire stems (woods) ; and (2) endogenous stems (straws and bamboo), and leaves (esparto). In this more miscellaneous group also we should include the refuse from the preparation of textile fibres, such as the root ends of jute (butts), the waste from the flax-scutching process (*infra*), &c.

We have already excepted the cotton fibre from the above classification, indicating a structural as well as a physiological distinction from other textile fibres. These are, in fact, always obtained and spun in the form not of *ultimate* fibres, but of bundles of these. The ultimate bast fibre is also a hollow tube, but more or less

thick walled and with tapering extremities ; in section it is seen to be cylindrical or polygonal. The dimensions are remarkably uniform for the bast of any given plant or species, but exhibit wide variations from species to species. Thus the average length of the bast cell of jute is 3 mm., and of flax 28 mm. The textile ' fibres ' are aggregates of these ultimate fibres, and it is convenient to employ for them the special designation of *filament*. This complex spinning unit varies in the number and degree of cohesion of the constituent fibres. These variations even in the same plant or species are very considerable, but more so as we pass from species to species. Expressed in another way, the textile fibres vary very much in regard to fineness and divisibility of the filaments. These, it is scarcely necessary to say, determine in a very important sense their spinning qualities. The nature of the fibre substance is a self-evident factor of the mechanical properties of the filaments ; and lastly, though less obviously, the length of the *ultimate fibre*, which greatly influences the strength and durability of the yarn.

To the spinner the chemical composition and properties of the fibre substance may appear of altogether secondary importance ; but they are obviously of first importance in regard to the application of the yarn, as of the goods woven from it. Supposing them put into use without further preparation, the durability of the fabrics will depend upon their resisting the disintegrating action of air (oxygen) and water, reinforced by heat and light. But a large proportion of the textile fabrics of commerce are supplied to the consumer in the bleached state, the process of bleaching consisting in the removal, by a more or less drastic treatment with reagents of those fibre constituents to which the colour of the raw material is due. These processes being the subject of a special article, we shall not require to deal with them at all in detail. The principles underlying them, however, have a close and obvious connection with the properties of cellulose, and the relationships subsisting between the cellulose of the vegetable fibres and the non-cellulose constituents with which each is associated in the plant ; and from this point of view we proceed to give a short account of the

CHEMISTRY OF THE COMPOUND CELLULOSES.

There are many reasons for regarding cellulose and the non-cellulose constituents of vegetable tissues and fibre substances as united chemically. While this is certainly true of the cutocelluloses (*infra*) there is evidence that in the ligno celluloses the bond of union is rather that of mutual interpenetration or ' adsorption.' At the same time the combination is equally resistant to reaction as that of a union of ' residues ' in the strictly chemical sense. Taking cellulose as the constant, the basis of our classification of the compound celluloses will be the nature of the non-cellulose, the characteristics of which are as distinct as they are general. Physiologists recognise three ' modifications ' of cellulose in the plant, and these we term ' compound celluloses.' We shall find the distinguishing chemical features of the three groups of compound celluloses as well marked

as their functional correlations, and the corresponding classification has a 'natural' in addition to its chemical significance. We shall consider first the group which is of least, because of only incidental, importance in relation to our subject.

Cutocelluloses (Adipocelluloses). The protective tissues of plants, which are, moreover, cellular rather than fibrous, viz. cork and cuticle, are composed of a substance of marked water-resisting characteristics. In this property, as well as in empirical composition, the cuticular substance designated *cutose* by Fremy resembles many of the waxes. The following percentage numbers are the results of the analysis of the cuticle of the apple purified from wax and adventitious matters : C, 73·66 ; H, 11·37 ; O, 14·97.

Cork is not a simple substance, but contains a number of products, wax, fatty esters and anhydrides, proteid residues, and tannins, &c., associated with the matrix or skeleton substance, which is of the nature of cutose. Both cutose and cork yield a residue of cellulose when treated with special reagents (sulphites) for the resolution of its union with the wax-like non-cellulose. The latter[1] is resolved by boiling with strong solutions of the alkalis into two fatty acids, a solid acid designated *stearocutic* and a liquid called *oleocutic acid*. The investigation of these cuticular substances has not been sufficiently extended to warrant our entering into further detail in regard to their composition and properties We may regard them as compound celluloses resolved by alkaline saponification into cellulose and a mixture of fatty acids of peculiar properties, but altogether unknown constitution They may be conveniently grouped under the term *adipocelluloses*, which broadly expresses their chemical relationship As regards their distribution, they occur chiefly in the epidermal and cortical tissues of leaves and stems, but the observations of Fremy lead to the conclusion that they are by no means confined to these, and there is evidence of their presence, if only in minute proportions, in the fibres themselves , but their occurrence, chemically speaking, may be regarded as adventitious, the fibre substances belonging to essentially different classes of compounds. These adipocelluloses, moreover, in most of the technical applications of vegetable materials which come within the province of this article, have to be got rid of. An instance of an epidermal tissue (cutocellulose) used as such is the Raffia, which consists of the cuticular tissues of *Raphia ruffia*, which in horticultural work replaces the linden bast or 'bass' of a former age. A more exhaustive investigation of Raffia as a type of cuticularised tissue has established the constitution of the cuto-cellulose of the mixed tissue as an ester of an oxidised 'cellulose' and a fatty acid

$$C_{17}H_{32}O_3 = C_{16}H_{30}(OH) \cdot COOH$$
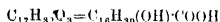
But investigations in this field are complicated by the resistance of the mixed tissues to proximate resolution ; the true cuto-cellulose when obtained is more or less modified by the chemical treatments required for its separation,

[1] According to Fremy, it is the cutose itself which is so resolved, but the author's experiments have always yielded a residue of cellulose.

and the yields are small (Cross and Bevan, J. Soc. Dyers, 1919, 35, 70).

When the textile fibres are isolated from compound structures this is accomplished for the most part by the mechanical processes of preparation, scutching, hackling, &c. When, however, the tissue intervening between the fibres and the cortex or epidermis is of small extent, the separation is never complete. In flax, for instance, residues of the epidermal tissue remain associated with the fibre, and the relative difficulty of attacking these substances by chemical means is a factor of the laborious process of bleaching linen goods. In isolating the so-called New Zealand 'flax' much greater difficulty is experienced. This fibre consists of the fibrovascular and other fibre bundles of the sword-shaped leaf of the *Phormium tenax*, and these are in such close and intimate contact with the epidermal tissues that their isolation is always very incomplete. In those raw materials of the paper maker which consist of the stems and leaves of monocotyledons (straw and esparto), the epidermal adipocelluloses constitute a sensible proportion. They are resolved in this case by chemical means, which require to be much more drastic in consequence. The fibrous portions of these materials, on the other hand, are made up of a compound cellulose belonging to the next group which we shall have to consider, an important characteristic of which is the comparative ease with which they are attacked and resolved by alkalis Although, therefore, the connections of these cuticular celluloses with the fibres are for the most part only indirect or incidental, we see in the typical instances above cited that they have to be taken into account in relation to a great number of the treatments of cellulose raw materials, both mechanical and chemical.

Pectocelluloses. Thus, the second division of the compound celluloses, is characterised by the non-cellulose constituents belonging to the group of *pectic* substances or *pectins*. The pectins are carbohydrate-colloidal aggregates or supposed complexes of hexosanes and pentosanes, with a small proportion of acid groups combined as lactone or ester. Sensitive to acid hydrolysis and ferment actions, they occur naturally in the most varied forms. Thus in fruit juices they exist as colloidal ropy solutions. In the more permanent fibrous tissues they are insoluble in water (Tollens, Annalen, 286, 278–292 ; Cross, Ber. 1895, 2609).

In composition they are more complicated than the celluloses, and they contain less carbon and more oxygen. In this and in many of their properties they resemble the oxycelluloses above described. Generally, they yield gelatinous hydrates, and under the action of hydrolytic agents they undergo a succession of changes resulting in the conversion of the comparatively inert members of the series pectose and pectin into highly acid derivatives, such as pectic and metapectic acids, bodies which, in addition to being acids, have properties indicating the presence of aldehydic groups.

The typical pectocellulose is the flax fibre. The purified bast of a Russian flax was found by Kolb to contain C, 43·7 ; H, 5·9 ; O, 50·4.

On boiling with dilute alkaline solution about 20 p.c. of its substance is readily converted into

soluble derivatives, of which a considerable proportion is a body identical with Fremy's pectic acid (C 42·0 p.c.; H=4·8; *i.e.* $C_{16}H_{22}O_{16}$). The fibrous residue from an exhaustive treatment with alkaline solutions, amounting in most flaxes to about 75 p.c. of the original weights, is approximately pure cellulose. In this experimental account of its constitution we disregard such adventitious admixtures as cuticular tissue (adipocellulose) and wood or 'sprit' (lignocellulose), the influence of which may be calculated and eliminated from the result; but the presence of these in commercial flax introduces complications of very great moment in regard to the spinning of the fibre and the bleaching processes to which flax goods are subjected. In regard to the latter, an important technical difficulty is experienced in washing flax yarns after a 'chlorine' (hypochlorite) bleaching treatment. 'Active chlorine' remains persistently in the goods. This is now elucidated, as due to the formation of *chloroamine* derivatives, from residues of chlorophyll and other nitrogenous products containing amino- groups always present in cuticular tissues (Cross, Bevan, and Briggs, J. Soc. Chem. Ind. 27, 1908).

Lignocelluloses. As the name indicates, this group comprises the substance of the ground tissue of the woods. The simplest type of lignocellulose, chemically as it is structurally, is the jute fibre, the lignified bast of an annual (*Corchorus tibuacæ*) cultivated on an enormous scale in India, and the staple of an important textile industry centred in Dundee.

The elementary composition of the purified fibre is expressed by the following percentage numbers:—

	Calc. for $C_{12}H_{18}O_9$
C=47·0-46·0 .	47·0
H= 5·9-5·7 .	6·0
O=47·1-48·3 .	47·0

The constitution of a lignocellulose is revealed by the action of chlorine, which combines with the non-cellulose or lignone component to form a quinone-chloride of constant composition, $C_{19}H_{18}Cl_4O_9$, with production of hydrochloric acid, also in constant proportion to the lignone; the estimation of the acid affords an indirect measure of the proportion of lignone or non-cellulose constituents (Cross and Bevan, Cellulose, Heuser and Sieber). The chlorolignone reacts with sodium sulphite (solution) to form a sulphonated derivative of characteristic magenta-red colour, freely soluble as sodium salt; consequently, the 'chlorinated fibre is resolved by treatment with solution of sodium sulphite (2 p.c. Na_2SO_3), the lignone-chloride dissolving from the cellulose, which is thus isolated. The quantitative constants of this reaction, which is specifically diagnostic, are as follows:—

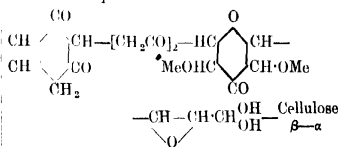|	P.c. of lignocellulose
Chlorine combining with lignone .	8·0
„ „ as HCl .	8·0

And the lignocellulose may be statistically calculated to be composed of:

	P.c. of lignocellulose	Carbon
Lignone $C_{19}H_{22}O_9$[C=57·8 p.c.]	20·0	11·56
Cellulose $C_6H_{10}O_5$[C=44·4 p.c.]	80·0	35·52
	100·0	47·08

The cellulose is separated actually as a hydrate of the composition $3C_6H_{10}O_5,H_2O$. It further differs from the normal cotton cellulose in being non-homogeneous. It is a mixture of two celluloses, the α-cellulose (65 p.c.), approximating to the normal, and β-cellulose (15 p.c.); the latter being relatively sensitive to hydrolysis and yielding a large proportion (40-50 p.c. of its weight) of furfural on boiling with condensing acids.

Constitution of lignone. The characteristic groups of the lignone complex are those which combine with chlorine and which appear to be of diketo r. hexene constitution. The reaction with bisulphites is also quantitative and the sulphonated derivatives are formed without resolution. Certain decompositions yield products quantitatively related to original groups: thus acetic acid is a product of oxidations both acid and alkaline, and appears to result from hydrolysis of ketene groups. By oxidation with CrO_3 in presence of hydrolysing acids the lignone is entirely resolved to oxalic and carbonic acids, with liberation of acetic acid. From the formation of volatile pyrone derivatives in the first stages of destruction, distillation (150°-200°), and from the statistics of ultimate composition, the presence of a pyrone group in the lignone complex is inferred.

An integral expression of these quantitative relationships is given in the form of a general statistical constitutional formula for the lignone-cellulose complex.

$$\mathrm{CH} \underset{\mathrm{CH_2}}{\overset{\mathrm{CO}}{\diagup}} \mathrm{CH-[CH_2CO]_2-HC} \diagdown \underset{\mathrm{CO}}{\overset{O}{\bigcirc}} \mathrm{MeOHC} \quad \mathrm{CH-} \atop \mathrm{CH\cdot OMe}$$

$$-\mathrm{CH-CH\cdot CH} \underset{\diagdown O\diagup}{\overset{OH}{\overset{}{OH}}} \quad \text{Cellulose } \beta\!-\!\alpha$$

(Cross and Bevan, Researches iii. p. 104). This has been critically examined by C. Doré in relation to the study of the action of ozone on the typical lignocelluloses (J. Chem. Soc. 103 (1913), 685) of the results of which it affords consistent explanations.

The wood substance of perennial woods (dicotyledons), with the same general characteristics, differs in the relation of lignone to cellulose, both in proportion and in mode of union. Whereas the jute fibre is attacked by solvent reagents similarly to the celluloses, the woods are extremely resistant. The following comparison of typical constants for beechwood is noteworthy:—

	Elementary composition		Proximate composition		Quantitative reactions of lignone		
	C	H	cellu-lose	lig-none	meth-oxyl	fur-fural	chlorine com-bining
Jute	47·0	5·9	80	20	4·6	8·0	8·0
Beech	49·1	5·6	55	45	6·2	12·8	12·0

The wood substance of the *Coniferæ*, first investigated by Erdmann (Ann. Suppl. 5, 223), is a homogeneous complex—lignocellulose—of empirical composition, $C_{30}H_{42}O_{21}$, differing in minor respects from the woods of angiosperms chiefly in the lower proportion of 'furfuroid' and acetyl groups. A reaction of fundamental import and general for the entire group of

lignocellulose, is the basis of the 'bisulphite' process of preparing cellulose from woods, applied chiefly to the coniferous woods, the insoluble residue of disintegration or cellulose constituting the most important staple of modern paper making. The lignone complex reacts quantitatively with the disulphites to form derivatives of the empirical composition $C_{24}H_{23}(OCH_3)_2O_3\cdot SO_3H$; the mechanism of the reaction being : (1) a hydrolysis of 'acetal' groupings due to combination of $H\cdot CO$ and bisulphite residues ; (2) the SO_3H residues then migrating to unsaturated $-CH=CH-$ positions ; the lignone complex being thus obtained as lignone sulphonates (Ca or Mg salts), which are gummy deliquescent solids.

These reactions take place progressively in the range of temperatures $80°$–$150°$, and industrially are carried out in digestors of special construction (silicate-lined) and enormous capacity.

A third reaction characteristic of the lignone complex as such and taking place in definite quantitative proportions is its condensation with phloroglucinol in presence of HClAq. There are two phases of the reaction : (1) with formation of a crimson colouring matter. This takes place with a proportion of the phenol less than 1 p.c. of its weight. The depth of colour is quantitatively related to the lignone, and is, therefore, an approximate measure of its proportion in a lignocellulose, as of lignocellulose (e.g. 'mechanical' wood pulp) in admixture with cellulose. (2) A further combination with the phenol (6–7 p.c. of its weight) to a product which is extremely resistant to hydrolysis (Cross, Bevan, and Briggs, Ber. 40, 3119 ; Cross and Bevan, J. Soc. Dyers, [v.] 32 (1916)).

Characteristic colour reactions are those with aromatic bases ; the anilines giving yellow to orange-colouring matters. Dimethyl-p-phenylenediamine give a deep-red colouration, which is the basis of the well-known quantitative method of estimating lignocelluloses in mixture (C. Wurster).

Ferric ferricyanide in solution is reduced by the lignocelluloses, and the intermediate ferroso-ferric blue cyanides in the highly hydrated colloidal form, are precipitated upon the fibre substance in intimate 'adsorption' combination. Jute fibre will take up from 30 to 50 p.c. of its weight of the blue pigments thus formed, without any change of essential characteristics These phenomena have especial interest in relation to theories of dyeing and the colloidal state (Cross and Bevan, J. Soc. Chem. Ind. 1893, 12, 104), and are of use in laboratory investigations of plant products (Sherman, J. Amer. Chem. Soc. 1897, 291).

The lignocelluloses have many-sided affinities for colouring matters, due to specific reactivities of the constituent groups of the lignone complex. They are dyed directly by dyestuffs of the most varied constitutional types ; and in this respect stand in marked contrast with the celluloses, which present a narrow and selective range of direct tinctorial capacity.

Other less characteristic reactions of the lignocelluloses may be briefly described.

Halogens.—Bromine reacts to form brominated lignone derivatives ; but the attack is much feebler than with chlorine, and is complicated

by oxidations (Cross and Bevan, J. Soc. Dyers, vol. 32, 1916). Cellulose is isolated by repeated treatments with bromine water, followed by dilute alkalis. This is a useful quantitative method of cellulose estimation (Hugo Müller, Pflanzenfaser). Iodine is absorbed from its aqueous solutions (in KI) in definite proportions. Jute fibre digested at $18°$ with 20 times its weight of N/10 solution as ordinarily prepared, absorbs 12·9–13·3 p.c. iodine (Cross and Bevan, Cellulose, 138, 139).

Hydrolytic agents generally attack the lignocelluloses as a whole, that is, without resolving the lignonecellulose combination. At elevated temperatures (100°–160°) dilute alkalis (NaOH, Na_2S) selectively attack the lignone groups, breaking them down to acid products—acetic acid, and the so-called lignic acids—which dissolve as sodium salts, and cellulose is obtained as a residue.

Dilute acids at higher temperatures yield acetic acid as a product of hydrolysis (Cross and Bevan, Cellulose, 160, 161 ; W. E. Cross, Ber. 1910, 43, 1526), and a complex of products of condensation, including furfural.

Oxy-hydrolytic agents attack the lignone complex owing to its unsaturated and oxidisable characteristics. By the action of nitric acid even in dilute form (5–10 p.c. HNO_3) and at low temperatures (70°–80°) the lignone is resolved into gaseous and soluble products ; the β-cellulose components are also attacked, and a residue of α-cellulose is obtained, but more or less oxidised to oxycellulose.

It is noteworthy that in presence of urea the action of nitric acid loses its specific character and resembles that of the simple hydrolysing acids (Cross and Bevan, Cellulose, 141, 145).

Chromic acid in presence of hydrolysing acids oxidises the lignone to oxalic and carbonic acids. Acetic acid appears as a product of hydrolysis (Cross and Bevan, J. Soc. Dyers, vol. 32, 1916). The insoluble residue is an oxycellulose soluble in large proportion in dilute solution of sodium hydroxide.

Permanganates in sufficient proportion oxidise the lignone complex to products of low molecular weight, but the action may be regulated and graduated to produce valuable bleaching effects.

Hypochlorites are used in industrial bleaching operations (jute yarns and fabrics), but require most careful control to prevent chlorination of the fibre substance, the fixation of chlorine, even in minute proportion, leading to ultimate disintegration of the lignocellulose (Cross, Bull. Mulhouse, 1883).

Ultimate oxidations. By 'fusion' with the alkaline hydroxides at 250°–350° the lignocelluloses are oxidised to oxalic acid, the yields from the wood (sawdust) being large (80 p.c.). The process is of considerable industrial importance, being the main source of the oxalic acid of commerce.

By chromic acid in presence of sulphuric acid the lignocelluloses are oxidised to gaseous products (CO_2 and some CO) and water. The reaction is the basis of a quantitative volumetric method of estimation.

Synthetical reactions. Esters. The lignocelluloses react, as do the celluloses, to form nitrates, acetates, and benzoates ; these, how-

ever, are mainly reactions with the cellulose of the complex, the lignone groups containing no reactive OH groups: these remain in condensed combination in the resulting ester complex.

The xanthogenic ester which results from the successive action of sodium hydroxide (17·5 p.c. NaOH solution) and carbon disulphide is a mixture or series of products, partly soluble, partly a highly hydrated and distended fibrous colloid which may be separated by filtration. There is little resolution or separation of the lignone groups from the cellulose.

Destructive distillation. The highly complex changes which the lignocelluloses undergo when heated out of contact with the air, are only approximately accounted for in terms of the original substance. Typical of an enormously diversified series of volatile products are:

Methyl alcohol	Methyl furfural
Acetone	Methyl- and methoxy-
Acetic acid	derivatives of Pyro-
Furfural	gallol

which may be regarded as direct products of resolution of the lignone complex.

Of great industrial importance are the products of the first group. The solid residue (about 30 p.c.) is wood charcoal, a highly condensed 'pseudo-carbon' of the approximate elementary composition, $C_{30}H_{18}O_4$.

Autoxidation of lignocelluloses. Lignocelluloses in the form of ground wood or 'mechanical' wood pulp are largely used in modern printing papers. Such papers are not only inferior in physical quality—tensile strength and elasticity —but in permanency; they change in colour (to yellow and brown) and in structure, becoming brittle. These are primary effects of oxidation; they are influenced by light, and by catalysts such as iron compounds usually present in papers as an incidental impurity, and resin acids added as sizing agents. These effects and defects are generally recognised and lead to the specific exclusion of 'mechanical' pulps from papers intended for documents of permanent value (Report of Society of Arts Committee on Deterioration of Papers, J. S. A. 1898).

An important elucidation if these phenomena is suggested by the researches of the late W. J. Russell, described in the Royal Society papers on The Action of Wood on Photographic Plates in the Dark (Phil. Trans. (B), 1904, 197, 281 ; Proc. Roy. Soc. 78, 385 ; 80, 346). The action in question is a 'photographic' image reproducing the structural details of the wood sections, placed at some distance from ordinary sensitive plates, but with exclusion of light

On the evidence, the effects are due to an 'active emanation' from the wood substance, which appears to be a product having the characteristics of hydrogen peroxide. The general evidence also connects the phenomena with those of autoxidation, and these again with the constitution of the lignone groups of the wood substance.

ASSAY OF FIBROUS MATERIALS.

For the investigation of fibrous raw materials in the laboratory the following scheme, devised by the author (Ind. and Col. Exhibition Reports, 1887), has been generally adopted :—

Separate portion taken for each determination. Results calculated in percentage of dry substance.

1. Moisture :
   Hygroscopic water, or water of condition, loss on drying at 100°.
2. Ash :
   Total residue left on ignition.
3. Hydrolysis :
   (a) Loss of weight on boiling 5 minutes in 1 p.c. solution of caustic soda ;
   (b) Loss of weight on continuing to boil one hour.
4. Cellulose :
   Isolation and estimation as previously described (chlorination method).[1]
   In the case of raw materials containing cutocelluloses the alkaline saponification is intensified by substituting alcoholic (2 p.c. NaOH) for the aqueous solution of sodium hydrate.
5. Mercerising :
   Loss of weight on treating one hour with strong solution of caustic soda, 15–20 p c. NaOH, in the cold.
6. Nitration :
   Weight of nitrated product, obtained by treatment with mixture of equal volumes of nitric and sulphuric acids one hour in the cold.
7. Acid purification :
   Loss of weight after boiling with 20 p.c. acetic acid and washing with water and alcohol.
8. Carbon percentage :
   Determined by combustion.

1a. Moisture. The mere operation of drying at 100° determines 'molecular changes in such compounds as the lignocelluloses, changes which affect the subsequent action of reagents. It is necessary, therefore, to weigh separate portions for the particular experiments in the air-dry condition, and calculate the dry contents from the data of the specimen weighed after drying at 100°. The dried specimen is treated for *1b Fat, wax,* and *resin.* These constituents are estimated as an aggregate extract obtained by boiling out with hydrocarbon solvents, or with ether-alcohol.

2. *Ash.* The specimen weighed after extracting may then be burned for the determination of ash. The ash in isolated fibres is low, viz. 1–2 p.c. ; in fibre aggregates it is often high, thus in esparto and straw from 3–6 p.c., and should be taken into account in calculations of yields or loss of weight. In such cases, after weighing the product of any given reaction the specimen or a portion of it should be burnt and the ash determined. The ash-free product is calculated in terms of the original substance, also taken ash-free.

The ash constituents are : (1) those of the normal fibre ; and (2) in certain cases adventitious mineral matter. These are easily distinguished and separately estimated.

3. *Alkaline hydrolysis.* This is the first stage of

[1] After lengthened critical investigation and discussion (1895–1918) the method of chlorination is generally adopted as the standard process of estimating 'cellulose '—with variations in treatment in special cases (dense lignocelluloses—cutocelluloses) and reservation as to the definition of 'cellulose' to include furfural-yielding components. For Bibliography, see W. H. Dore, J. Ind. & Eng. Chem. ii (1919), 556.

towards the isolation of the cellulose. When the numbers obtained for the short period (*a*) and for the long digestion (*b*) show a marked difference, it is an obvious general indication of low paper-making quality.

4. *Cellulose.* Having isolated a white residue from a raw fibrous material, it may be weighed and then further investigated. An estimation of furfural will establish its position in the classification of the celluloses. For practical purposes it is sufficient to establish the degree of resistance of the cellulose to further alkaline hydrolysis, and to oxidation by alkaline cupric oxide (Barreswil's or Fehling's solution).

5. *Mercerising* The effect of the action of caustic soda as measured by loss of weight, and also changes in appearance and structure, may be usefully observed on the isolated celluloses, and in certain cases upon the raw fibrous materials. The pectocelluloses are considerably gelatinised by the treatment, the fibres often undergoing agglomeration and drying to a harsh wiry condition. The lignocelluloses are effected in the contrary direction The cutocelluloses are not attacked.

From all the above treatments the products should be treated with dilute acids by immersion in the cold, and copiously washed before drying. The drying is accelerated by treatment with alcohol.

6. *Nitration*, or conversion into nitric esters, affords useful information ; but judgment must be exercised as to the applicability of the treatment to the raw material, to the partially purified products (alkaline hydrolysis), or the isolated cellulose. It is a general measure of the proportion of reactive alcoholic OH groups, and also of resistance to oxidation.

7. *Acid purification* removes basic mineral matter, often present in some quantity in raw materials, of the pectocellulose class. It may sometimes be required to attack and remove more resistant mineral constituents, such as silica or silicates. In this case the material may be digested with a mixture of hydrofluoric and hydrochloric acids in vessels suitably resistant to the action of these acids. The treatment is followed by copious washing.

8. *Carbon percentage.* This is only necessary in certain investigations. The value of the constant will be recognised from the fact that it varies considerably for the different groups of compound cellulose. The most convenient method is that of combustion, with chromic acid, after solution in sulphuric acid.

For special purposes the above scheme is extended by operations on a larger scale, and under conditions which approximate to those industrially employed, as, for instance, in estimating the value of a raw material for paper-making purposes : complementary investigation of structural characteristics, including the measurements of length and diameter, of ultimate fibres (cellulose) is also required. For processes and methods the special text-books must be consulted.

The following is a general view of the

CELLULOSE INDUSTRIES.

Celluloses, fibrous material, used as such :
(1) *Mechanical* with *incidental chemical treat-*

ments (bleaching, dyeing, mercerising finishing) :
Textiles, fine fabrics :
  Cotton, flax, hemp, ramie.
Coarse textiles :
  Jute (flax and hemp).
Ropes, twines :
  Hemp flax, manilla, aloe, and fibres of monocotyledons
Hat-making materials :
  Straw, wood.
Paper, boards, and fibrous agglomerates :
  Cotton and linen rags and textile wastes (wood, straw, esparto pulps).

(2) *Chemical industries.* Cellulose derivatives, or celluloses, or products of resolution of compound celluloses.
Explosives :
  Nitro celluloses.
Artificial fibres :
  Nitro celluloses (acetates).
  Aqueous solutions of cellulose derivatives.
  Zinc   chloride,   cuprammonium, xanthogenic ester (viscose)
Films or sheets :
  Nitrocellulose (acetates), xanthogenic ester.
Massive solids :
  Nitrocellulose (acetates), xanthogenic esters.
Preparation of wood pulp, esparto, straw, and other celluloses for paper making :
  Treatment of coniferous woods, esparto, straw, and textile waste materials.

(3) *Products of decomposition* :
Oxalic acid :
  Fusion of wood wastes with alkaline hydroxides.
Acetic acid, wood spirit, acetone, creosote, charcoal :
  Products of destructive distillation of woods.

Supplementary Note. (Jan. 1, 1920)

The chemistry of ' cellulose ' is obviously a section of the ' chemistry of colloids ' ; the state of development of this extensive and complex subject is set forth in the Reports (I, 1918 ; II, 1919) of the British Association Committee. Cellulose is in many respects the prototype of the organic colloids ; as a primary natural product it is only known to us in its natural forms of organised structures ; and it is an index of the necessary trend of progressive research in this field that the works of the histologist and chemist are convergent. Thus : W. L. Balls (Proc. R. S (B.) 1919, 90, 542) demonstrates daily growth rings in the cell wall of cotton by taking advantage of the xanthic ester reactions under limiting conditions, such as induce controlled rehydration of the cell substance without disruptive distortion.

Robinson (Prov. Rep. R. S. Proc. Nov. 1919), in investigating the deformation of wood structures under stress, finds positive evidence of associated deliquification in the chemical sense.

Cross and Bevan (J. Soc. Dyers, 1918, 34,

215, 247) have investigated two cases °of profound structural change in cotton under mechanical stresses, associated with fundamental changes of chemical constitution.

Of these effects the immediate factor of change may be a particular form of energy, in respect of which the effects of heat, electricity, light, and radio-active 'matter,' have been shown to be definitive (*ibid.*; and S. J Lewis, 34, 167; W. Harrison, 1919, 35, 243–250)

It is clear that for exact characterisation of cellulose, as a colloid, it must be investigated as such, and not in terms of products of proximate resolutions. This postulates physical methods, of which the most obvious is the measurement of volume and volume changes (Cross and Bevan, Berl. Ber. 1909, 42, 2198), with temperatures and under reaction Such investigations have already suggested that the cellulose may be made up of reactive unit groups of small dimensions—of cyclic configuration—and having the reactive continuity of liquid systems Research and progress by way of such problems and hypotheses, many of which arise in the technical routine of the cellulose industries, are the leading characteristics of the present-day movement towards a more comprehensive science of the subject

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CELTITE *v.* EXPLOSIVES.

CELTIUM Ct. At. wt. ? An extremely rare element intermediate in characters between lutecium and scandium, occurring in gadolinite and first isolated by Urbain. Forms a white oxide, and an anhydrous chloride more volatile than lutecium chloride, but less volatile than scandium chloride. The hydroxide is a weaker base than lutecium hydroxide, but is stronger than scandium hydroxide. Gives a characteristic arc spectrum (Urbain, Compt. rend. 1911, 152, 141)

CEMENT. In this article the word 'cement' is used to mean a calcareous compound employed in building, and does not refer to minor adhesives of the class typified by glue.

Portland cement. This material is so greatly more important than any other cement of its class, that it may appropriately be dealt with first. The name is trivial, referring merely to the colour of the set product which somewhat resembles that of Portland stone. The invention of Portland cement is attributed to Aspdin of Leeds, who calcined a mixture of chalk and clay, and found that the product, when ground and mixed with water, would set; but development from this elementary stage to the status of a valuable industry was the work of many minds, which, practising mostly empirically, arrived at a procedure competent to ensure a commercially useful product, although by methods of which the *rationale* was only dimly understood. At the present time, a better state of knowledge exists, and except in a few minor points, such as the adjustment of the setting time, which still cannot always be completely controlled, the manufacture is performed with precision and the product is of uniform and excellent quality. Nevertheless, the chemistry, both of the formation of Portland cement from its raw materials and of the changes which it undergoes on setting, is incomplete, many of the reactions supposed to occur remaining obscure and hypothetical.

Composition.—Portland cement consists of a mixture of compounds of lime and silica and of lime and alumina. These are the essential constituents, but it commonly contains in addition loose compounds of lime with ferric oxide, magnesia, and small quantities of inert insoluble silica or silicates. alkalis and sulphates. Except when perfectly calcined and absolutely fresh, it also contains a little water and carbonic anhydride absorbed from the air. The ultimate composition of Portland cement varies with the nature of the raw materials from which it

has been made. The following is a typical analysis of cement made from chalk and clay in the Thames and Medway district :—

	Per cent.
Silica (SiO$_2$)	22·0
Insoluble silicious matter . .	0·7
Alumina (Al$_2$O$_3$) . . .	6·5
Ferric oxide (Fe$_2$O$_3$) . . .	3·3
Lime (CaO)	63·0
Magnesia (MgO) . . .	1·0
Sulphuric anhydride (SO$_3$) . .	1·5
Carbonic anhydride (CO$_2$) . .	0·5
Water (H$_2$O)	1·0
Alkalis	0·5
	———
	100·0

All the constituents may depart a good deal from these proportions. The silica may vary from 18 to 27 p.c., the alumina from 5 to 10 p.c., the ferric oxide from nil to 7 p.c., the lime from 58 to 67 p.c., the magnesia up to 3 p.c., the sulphuric anhydride up to 2·75 p.c., the alkalis to 2 p.c., and the water and carbonic anhydride according to the length of time the cement has been made and the extent to which it has been exposed.

The limits laid down by the British Standard specification are as follows · The proportion of lime to silica and alumina shall be not greater than the maximum nor less than the minimum ratio (calculated in chemical equivalents) represented by $\dfrac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 2\cdot85$ or $3\cdot0$ respectively. The percentage of insoluble residue shall not exceed 1·5 p.c , that of magnesia shall not exceed 3 p.c.; and the total sulphur content calculated as sulphuric anhydride (SO$_3$) shall not exceed 2·75 p.c. The total loss on ignition shall not exceed 3 p.c.

Although the ultimate composition of Portland cement is easily and accurately ascertained by the ordinary methods of chemical analysis, its proximate composition, that is, the nature and quantity of the chemical compounds or physical mixtures which constitute it, are not known with exactness and cannot be determined with precision by existing methods of inquiry. The view most in favour and best supported by experimental evidence, is that the essential constituent is tricalcium silicate 3CaO·SiO$_2$, and that the body next in importance is a calcium aluminate, to which the formula 2CaO·Al$_2$O$_3$, or alternatively

$$3\text{CaO·Al}_2\text{O}_3,$$

is assigned. Dicalcium silicate 2CaO·SiO$_2$ is also present. The oxide of iron occurs as a calcium ferrite, the magnesia possibly as such, the sulphuric anhydride and carbonic anhydride probably as calcium sulphate and carbonate, and the alkalis perhaps as double compounds with lime and silica or alumina. As far as is known, the substances of primary importance are the tricalcium silicate and aluminate only, the minor bodies being little more than makeweights with the exception of calcium sulphate, which is of moment, because of its influence on the setting time of the cementitious constituents proper. The best proof that these smaller constituents are not essential is afforded by the fact that Portland cement of the highest quality can be prepared containing only silica, alumina, and lime in proper proportions.

It was formerly held that the calcium aluminate and silicate did not exist separately but as solid solutions, which are recognisable as distinct minerals in Portland cement clinker. The mineral termed *alite* is a solid solution of tri- (or di-) calcium aluminate in tricalcium silicate, whilst the solid solution of dicalcium aluminate in dicalcium silicate is called *celite*. As both are solid solutions and not definite compounds, their composition is not constant, but varies within the limits of solubility of the solute in each case. Celite appears to be almost inert, and to take little part in the setting of the cement, but alite is decomposed by water, and both the calcium silicate and calcium aluminate are hydrated according to the following equations, in which, for simplicity, the two substances are dealt with separately :—

(1) 2(3CaO·SiO$_2$)+9H$_2$O=2(CaOSiO$_2$)5H$_2$O+4Ca(OH)$_2$).
Tricalcium silicate   Hydrated monocalcium silicate.

(2) 3CaO·Al$_2$O$_3$+12H$_2$O=3CaO·Al$_2$O$_3$12H$_2$O.
Tricalcium aluminate   Hydrated tricalcium aluminate.
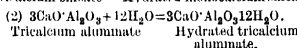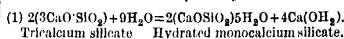
It will be seen that in the process of hydration of the tricalcium silicate, two-thirds of the lime are liberated and appear as calcium hydroxide, and in consequence this substance forms a large proportion of Portland cement when set; although—accepting the tricalcium silicate view—uncombined lime is absent from Portland cement as it comes from the kiln.

The belief that tricalcium silicate is the essential constituent of Portland cement has been disputed on the ground that there is no conclusive proof of the existence of this body as a definite chemical individual. The alternative theory is that the essential constituent is dicalcium silicate 2CaO·SiO$_2$, associated as a solid solution with lime, which may be present in amount equal to that occurring in the tricalcium compound. On this assumption, the equations written above would still stand with the modification that this part of the lime is hydrated directly on setting, instead of being both liberated and hydrated by the action of water. Whichever view may be nearer the truth, it is certain that set Portland cement contains large quantities of calcium hydroxide, a fact which has an important practical bearing in the use of the material, as will be shown when dealing with puzzolana.

Since the time when this idea was put forward the older view has been rehabilitated by the preparation of tricalcium silicate as a definite compound, and that it and tricalcium aluminate are the two substances to be considered as the essential constituents of cement. It follows that the equations originally put forward by Le Chatelier may be taken as representing the process which cement undergoes on setting :—

3CaOSiO$_2$+Aq=CaOSiO$_2$2½H$_2$O+2Ca(OH)$_2$
and

3CaOAl$_2$O$_3$+Ca(OH)$_2$+Aq=4CaOAl$_2$O$_3$12H$_2$O
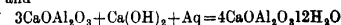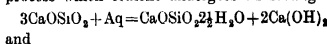
It will be seen that the hydration of the tricalcium silicate provides ample calcium hydroxide for the production of tetracalcium aluminate, and as stated above the existence of this calcium hydroxide in set Portland cement is of importance when siliceous materials such as puzzolana are used conjointly with cement,

Manufacture.—As would be expected from what has been said concerning the composition of Portland cement, the raw materials from which it can be prepared are of the most varied description. Chalk, limestone, or any other approximately pure form of calcium carbonate on the one side, and clay, shale, or any typical argillaceous material on the other, can be mixed and burned together to produce Portland cement, provided that the product has a composition falling within the limits already laid down. It follows naturally that substances which contain both calcium carbonate and clayey matter, such as calcareous shales and argillaceous limestones, can be similarly used. On this account and because of the low price of the manufactured article and the consequent high proportion which freight bears to the total cost at the point of consumption, the manufacture of Portland cement is not confined to a particular spot, but is successfully undertaken wherever deposits of suitable raw materials occur, provided the cost of fuel is not extravagantly high. But although it is perfectly practicable to manufacture Portland cement from a wide range of raw materials, yet certain of these possess qualities which give them a substantial advantage. The large deposits of chalk in the Thames and Medway district, together with the clay in the form of river mud adjacent thereto, make this region one of the centres of the industry in this country In like manner, the existence of huge quantities of argillaceous limestone in Pennsylvania has led to the establishment of many large works in that State In the former case, the chalk and clay, being soft materials, can be readily handled and intimately mixed, and in the latter the mingling of the calcareous and argillaceous ingredients has already been accomplished, and a correct composition can be attained by the addition of a small amount of pure limestone

The following are analyses of some of the raw materials commonly employed :—

Chalk.

	Per cent.
Moisture	19 03
Sand and clay	0·93
Combined silica (SiO_2)	0 43
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	0 48
Lime (CaO) [1]	42·90
Magnesia (MgO)	0·42
Carbonic anhydride (CO_2)	34·16
Alkalis, organic matter, and loss	1·65
	100·00

Clay.

	Per cent.
Sand	28·42
Combined silica (SiO_2)	30·32
Alumina (Al_2O_3)	15·49
Ferric oxide (Fe_2O_3)	7·74
Lime (CaO)	2·04
Magnesia (MgO)	1·96
Sulphuric anhydride (SO_3)	1·96
Combined water and loss	12·07
	100·00

[1] Corresponding with calcium carbonate ($CaCO_3$) 76·60 p.c.

Limestone.

	Per cent.
Insoluble silicious matter	0·20
Alumina+ferric oxide ($Al_2O_3+Fe_2O_3$)	0·08
Lime (CaO)	56·02
Magnesia (MgO)	0·24
Carbonic anhydride (CO_2) [1]	43·38
Combined water and loss	0·18
	100·10

Shale.

	Per cent.
Silica (SiO_2)	60·22
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	27·20
Lime (CaO)	trace
Magnesia (MgO)	1·62
Carbonic anhydride+water (CO_2+H_2O)	4·54
Alkalis and loss	6·42
	100·00

Marl.

	Per cent.
Silica (SiO_2)	15·10
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	7·30
Lime (CaO)	42·16
Magnesia (MgO)	0·34
Carbonic anhydride (CO_2)	33·51
Water, alkalis, and loss	1·59
	100·00

Whatever may be the raw materials, the first step in the manufacture of Portland cement is to secure their comminution and intimate admixture. It must be understood that as the process of burning cement involves the sintering but not the fusion of the materials, these two conditions are of primary importance. The raw materials are commonly ground so that they leave a residue of less than 10 p.c. on a 180×180-mesh sieve, and intimacy of contact is secured by mixing the materials together at as early a stage of the process of comminution as is practicable, and in addition grinding them together. The procedure is as follows : In the case of soft, wet raw materials, such as chalk and clay, the two substances in proportions determined from their analysis are weighed into a wash mill, which is a large tank in which a vertical spindle having radial arms from which depend harrows is caused to revolve. Enough water is added to allow the materials, when well beaten up, to form a thick cream or slurry, which is mobile enough to flow and to be pumped. The slurry passes through screens to retain stones and grit, and is ground either between millstones or in more modern practice in a tube mill, which is a cylinder made of steel lined with a hard material such as quartzite blocks and partly filled with flint pebbles. The cylinder is set horizontally and revolved, the slurry being fed in through a trunnion and passing out at the other end. During its passage through the cylinder, it is ground by the pebbles which are continually raised up the periphery of the cylinder and continually drop back through the liquid mass, pounding its particles on the lining of the cylinder and between the pebbles themselves. After being thus ground, the slurry flows into large reservoirs, called dosage tanks, where it is sampled and

[1] Corresponding with calcium carbonate ($CaCO_3$) 98·36 p.c.

analysed and, if necessary, its composition is corrected by the addition of more chalk or clay. In the early days of the industry, the slurry was prepared with so large a proportion of water as to be a thin cream from which the water was allowed to settle in large tanks, the supernatant water being drawn off and the deposited solids dug out when they had arrived at the consistency of mud, and this method is still occasionally practised. Usually, however, the quantity of water used is the least that will allow the slurry to flow (35 to 50 p.c. of the weight of the slurry, according to the nature of the raw materials),adequate mixture being thus obtained and the delay and cost of double handling avoided. The next step is to dry and burn the slurry to clinker. The modern method combines these operations, the slurry being pumped into the upper end of a rotatory kiln (see below), where it is dried and burned as it travels down the kiln. Before the invention of the rotatory kiln, drying was effected either by the heat of coke ovens used for manufacturing the coke needed in the subsequent burning or by the waste heat of chamber kilns (see below), the mass thus dried cracking into rough cakes suitable for loading into the kiln Where the kiln was of a type which provided no surplus heat, the slurry was dried independently, crushed, and moistened with a little fresh slurry, moulded into bricks, redried and burnt The choice among these various procedures depends on the kind of kiln for which the slurry is destined.

When dry raw materials such as limestone and shale are used, they are crushed in a stone breaker or between rollers, according to their hardness, any moisture such as quarry water or damp from exposure to weather being removed by passing through rotating cylinders, heated by flue gases, or by an independent fire or in towers through which hot air is blown, and are ground together in the calculated proportions. The grinding is performed by ball mills, consisting of a drum lined with perforated steel plates and partly filled with steel balls, followed by a tube mill, such as has been described above, or in mills of the Huntingdon class, in which rollers depending from spindles attached to a vertical axle are driven outwards by centrifugal force as the spindle is rotated and bear against a steel grinding ring between which and the rollers the material is ground. It will be understood that many different forms of comminuting apparatus can be and are used in cement works, according to the nature of the material. Discussion of their relative merits would be out of place in an article of this kind. The dry raw materials are fed as powder (often slightly damped to prevent dust) direct into a rotatory kiln or are moistened sufficiently to allow them to be moulded into bricks, dried and burnt in one of the kinds of fixed kiln.

Although wet raw materials are naturally ground wet, and dry raw materials are ground dry, yet occasionally dry raw materials are ground wet, it being maintained by some that any extra expenditure of heat to drive off the water added is compensated for by the more intimate admixture of the raw materials and the ease with which the slurry may be conveyed by being pumped or allowed to flow in contrast to dry raw materials which require elevators, worm conveyors and similar mechanism.

The raw materials finely ground, intimately mixed and in correct proportion (containing in most cases about 75 p.c. of calcium carbonate calculated on the dry substance, the balance being the clayey constituents) are burnt to cement clinkers in various types of kiln.

The earliest was the bottle kiln, a dome-shaped brick structure lined with fire bricks, having a short chimney and a grate. The lumps of dried slurry were loaded into this, mixed with coke, and the charge fired and allowed to burn out, the products of combustion escaping at the top of the kiln An improvement on this is the chamber kiln shown in Fig. 1. It is a cup-shaped structure, lined with fire brick, in which the dried slurry and coke are placed in layers, communicating with a wide flue, which forms a floor on to which wet slurry can be run, the far end of the flue being connected with a chimney stack The hot gases from the kiln proper pass over the slurry and dry it, so that a charge is ready when the previous one is burnt. An ordinary chamber kiln will produce about 30 tons of clinker per run, which, including
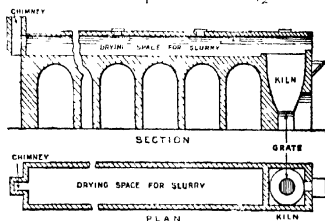

FIG. 1.—CHAMBER KILN.

loading and discharging, usually takes a week, and it will burn 40–50 p.c. of coke, reckoned on the weight of clinker produced. The coke is generally bought from gas works, though formerly coke ovens were in use at the cement works themselves, the products other than coke being wasted. As the coke and raw materials are mixed in the kiln, the ash of the coke appears in the finished cement, raising the proportion of silica appreciably, on this account it is customary to use raw materials containing a higher percentage of calcium carbonate in a kiln of this kind than in one in which the whole of the ash is not retained, so as to compensate for the added siliceous matter, but even with this precaution the product is irregular, the ash attaching itself chiefly to the outside of the clinker and not penetrating to the centre of the lumps. It is impracticable to burn the material uniformly. Parts will be almost fused, parts merely lightly calcined and decarbonated, barely sintered and not truly clinkered, while yet other parts will have attacked the silicious lining of the kiln, forming with it a sort of slag. Hence it is necessary to pick the charge when it is drawn, rejecting the underburnt and the slagged material, and on the perfection of this picking the quality of the finished cement largely depends.

The shaft kiln is another type of fixed kiln

in which the fuel is mixed with the raw material. There are various forms of shaft kiln, but the principle is the same in all cases, the raw material and fuel proceeding vertically down a shaft to a point where combustion occurs, and passing from this down a continuation of the shaft to a drawing hole from which the clinker can be extracted. Loading and drawing proceed regularly, the kiln working continuously instead of intermittently, as does the chamber kiln. The working is regenerative in the sense that the products of combustion from the burning zone pass up through the unburnt raw material, which is thereby heated and the air for combustion flows through the hot clinker in the lower part of the kiln, and thus is heated before taking part in the combustion The Schneider and the Aalborg kiln are examples of this type, the latter is shown in Fig 2 Another well-known shaft kiln with the modification that the upper and lower parts of the shaft are not in the same vertical line, is the Dietsch kiln (Fig 3) In this, the heated raw material is received on a stage between the upper and lower part of the shaft and passes thence into the burning zone. In the illustration, two such kilns are shown, built back to back. There are various modifications of the shaft kiln differing in details of design, some working with forced draught From their regenerative mode of working, they are economical of fuel, but require a good deal of moderately skilled labour and give a product mixed with the ash of the fuel and requiring picking.
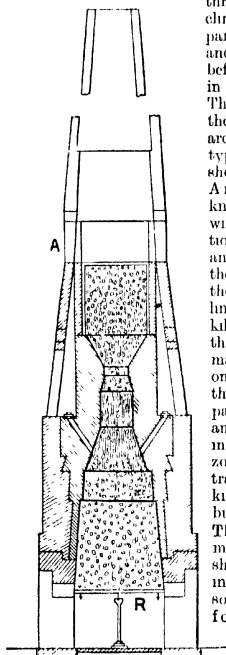
The Hoffmann or ring kiln (Fig. 4), largely used for brick making, is also used in the manufacture of cement. The materials are moulded into rough bricks, and these are stacked in chambers arranged round a chimney which serves them all. Fuel is distributed between the blocks, and the working of the kiln is systematic, continuous, and regenerative. Passage from one chamber to another and to the chimney can be controlled, and thus burning can be carried on in one chamber while the air for combustion flows in through hot clinker in chambers in which burning has been finished and the

FIG. 2.—AALBORG KILN.

hot gases from the burning chamber heat the raw material in chambers ahead of it on their way to the chimney, the chamber representing the locus of combination continually shifting forward step by step all round the ring. As might be expected, this kiln is economical of fuel, but costly in labour for loading and unloading
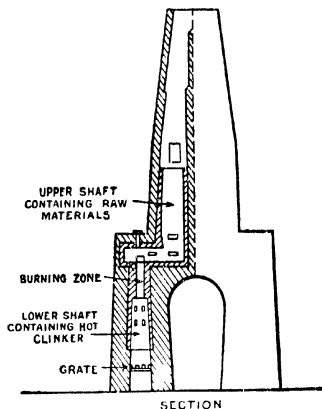
FIG. 3.—DIETSCH KILN.

the chambers, and yields a product lacking uniformity.

In modern practice, these various kinds of fixed kiln have been displaced by the rotatory kiln, which, though originating in thi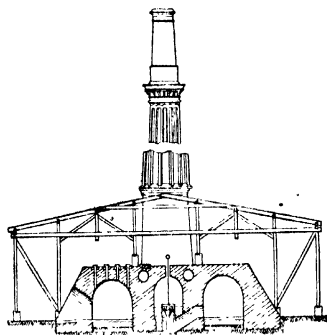s country, was brought to a working success in the United States, and began to be adopted here and on the Continent about 1898. This kiln is a steel cylinder lined with fire brick, set at a small angle with the horizontal, and capable of being slowly rotated round its axis. At the upper end the raw material is fed in, and at the lower is a burner sufficiently powerful to reach a clinkering temperature (about 1400° C.). As the cylinder rotates, the raw material travels

FIG. 4.—HOFFMAN KILN.

down the cylinder on account of the inclination, and on its journey is gradually raised in temperature until it reaches the lower end, where it is clinkered and drops out. The process is continuous, systematic, and to a considerable extent regenerative. The labour required is small and the output large per unit of plant. A large proportion of the fuel ash passes through the kiln without attaching itself to the raw material, and such portion as remains is incorporated with the raw materials and forms part of the finished product instead of being largely confined to the surface of the clinker, as is the case with the product from fixed kilns. When burning is carried out properly, the whole of the product is uniformly clinkered and needs no picking, but may need quenching.

The earlier rotatory kilns were some 60 feet long and 6 feet external diameter. At the present time, an ordinary size is $200 \times 8\frac{1}{2}$ feet and larger have been made and used. The output of a single kiln of this size is as much as 1000 tons a week, according to its size, as compared with 30 to 70 tons a week for a fixed kiln. A rotatory kiln is run as nearly as possible day and night, including Sundays, throughout the year, stoppages being made only for repairs or to patch the coating of clinker which forms on the fire-brick lining of the kiln (Fig. 5). The kiln was formerly of uniform diameter, but modern designs are of larger diameter at the burning end, so as to provide a wider portion at the place where combustion is at its height. The earliest form of rotatory kiln which approached success, was fired with producer gas, but many difficulties arose in the use of this fuel, and although the idea has merits and has been revived, it has not reached fruition. Oil burners, like a large blast lamp, having the oil sprayed in by steam or compressed air, are used with complete success wherever oil is cheap enough, but as the cost is too high in most countries, powdered coal is the standard fuel. Coal, preferably bituminous, and containing a moderate amount (10 p.c.) of ash when well dried and very finely powdered, can be used to form a sort of blowpipe flame much as if it were a fluid, the powder being driven into the kiln by a blast of air and issuing from a jet much as gas might do, and burning there in a supply of secondary air supplied to the space around the jet and preferably pre-heated. In actual working, these conditions are realised in the following way : Small coal is dried in a rotatory drier heated by an independent fire or
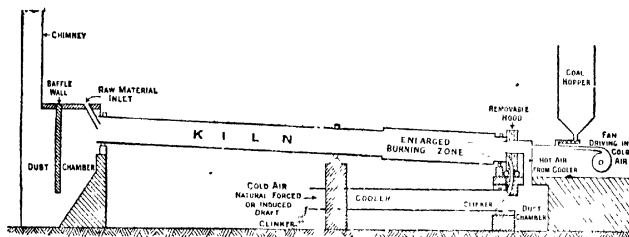

FIG. 5.

by the kiln gases. It is powdered very finely so as to leave not more than 5 p c. residue on a sieve having 180×180 meshes per square inch. This powdered fuel is fed from a hopper into a pipe through which air is driven by an air compressor or a fan, and issues from the mouth of this pipe, which passes through a shield or screen covering the lower end of the kiln, as a jet of dry finely powdered combustible matter carried by a blast of air, insufficient for its combustion and serving chiefly as a means for its propulsion in the form of a jet. This jet is set into the mouth of the kiln and pointing towards the far end. Air for the combustion is drawn in by the draught of the chimney stack, with which the upper end of the kiln communicates, and on its way passes through a rotating cylinder down which is proceeding the red-hot clinker issuing from the kiln, absorbing a portion of that heat, and carrying it to the place of combustion. By these means a powerful jet of flame is produced, the temperature of which is ample for clinkering.

Either dry or wet raw materials can be burned in a rotatory kiln. Dry materials are fed in by a screw, the mass being usually slightly damped by a small proportion of water in the trough in which the screw works, so that the fine dusty particles are not carried away by the draught of the kiln. Wet raw materials are simply allowed to flow in from a trough in which the height of the slurry is maintained constant by a device such as a pump, more than capable of the maximum flow, the surplus being returned by a by-pass. The water, about 40 p.c. of the weight of the slurry, is evaporated by the hot gases coming from the lower end of the kiln, and the dried slurry forms itself into small nut-like masses as it rolls round the inside of the cylinder. These travel slowly downwards in a spiral path, and their temperature rises until the calcium carbonate is decomposed, the clay is dehydrated, and union begins between the acid and basic oxides, the silica, alumina, and ferric oxide acting in the first and the lime, magnesia and alkalis in the second sense, until finally the material becomes slightly plastic, and full combination is effected at a point near the lower end of the kiln, where the temperature is highest. The white-hot clinker passes into a cooler, such as the rotating inclined cylinder already mentioned in connection with the heating of the air necessary for combustion, where it is often sprinkled with water for the double purpose of completing its cooling and of hydrating any lime which may not have been perfectly combined in the kiln.

With dry raw materials the course of operations is the same, save that only the small quantity of water used to prevent dust has to be evaporated.

On account of the fact that cement clinker is a basic material and that fire brick is an acid substance, using those words in the ordinary metallurgical sense, interaction may occur between these at a clinkering temperature, and a slag may be produced. Any overheating will cause the rapid formation of this slag, with the result that the clinker will be spoiled and the lining destroyed. But if the burning is properly conducted, the action is not uncontrollable, and further can be prevented by the device of heating down the slightly plastic clinker on to the fire-brick lining, so that it adheres and itself forms the true lining, to which, of course, the rest of the clinker is chemically indifferent. The coating breaks away from time to time, and needs to be patched by beating down fresh clinker on the fire brick thus left bare. Linings of less acid substances such as bauxite, and basic linings such as magnesia bricks, have been tried, but all present some practical defect which makes them less suitable than fire brick used in the way described.

Good well-burnt clinker, whether made in a fixed or rotatory kiln, is a hard rock-like mass of dark colour, varying from brown to almost black. The pieces of clinker from fixed kilns are chiefly rough lumps of similar size to that of the blocks of raw material, and need a preliminary crushing in a stone breaker before they can be ground. The product from a rotatory kiln is in the form of small rounded masses, varying in size from a pea to a walnut. Sometimes a number of these will stick together, making a mass a foot or more in diameter, but the bulk of the product is small enough to be ground without previous crushing.

Grinding is effected in machines similar to those used for preparing the raw materials. Ball and tube mills and mills of the Griffin and Huntingdon class are in most general use, millstones, such as were used for grinding corn, having been superseded on account of their small output and heavy upkeep. The clinker is ground to cement having a residue of not more than 14 p.c. on a 180 × 180-mesh sieve, and is conveyed mechanically to warehouses where it is stored and bagged or filled into casks. In a modern works, the whole operation from the reception of the raw materials to the filling of the bags is conducted almost wholly mechanically, manual labour being eliminated as completely as possible, an object easily attained with rotatory kilns, which do not require to be loaded and unloaded by hand.

Testing Portland cement. The quality of Portland cement and its suitability for building purposes is ascertained by various mechanical tests and by its chemical analysis. The analysis shows whether the constituents fall within the recognised limits stated above, and detects the presence of such adulterants as blast furnace slag or Kentish rag (a silicious limestone), which differ widely from cement in composition or contain some characteristic constituent such as calcium sulphide, which is almost or wholly absent from Portland cement. But as it is impracticable to make a *proximate* analysis of Portland cement, the ordinary analytical figures will not indicate whether the raw materials have been sufficiently intimately mixed and sufficiently thoroughly burnt to form those cementitious substances constituting sound and serviceable Portland cement. This question can, however, be satisfactorily settled by physical and mechanical tests.

Codes of testing are in common use in all countries, and the following are the principal requirements of the British Standard Specification :—

The *fineness* to which the cement has been ground is a useful indication of quality, inasmuch as the coarser parts hydrate so slowly as to be of little or no cementitious value.

The residue on a sieve 180 × 180 = 32,400 meshes per square inch, shall not exceed 14 p.c.

The residue on a sieve 76 × 76 = 5776 meshes per square inch, shall not exceed 1 p.c.

The *specific gravity* of cement is a useful criterion, and shall not be less than 3·10. If below the normal value, say 3·10 to 3·15, according to the degree of aeration to which it has been subjected, it may generally be inferred that the cement has been underburnt.

The *mechanical strength* of cement is determined by ascertaining the tensile strain of briquettes of 1 square inch section made of neat cement, and also of cement mixed with three times its weight of standard sand.

The breaking strength of the neat briquettes 7 days after gauging shall not be less than 450 lbs. per square inch, and of the sand briquettes 200 lbs. per square inch.

The breaking strength of the briquettes at 28 days after gauging shall show an increase on the breaking strength at 7 days, and shall be not less than the number of lbs. per square inch of section arrived at from the following formulæ for neat and sand briquettes respectively :—

Breaking strength at 7 days
$$+ \frac{40{,}000 \text{ lbs.}}{\text{Breaking strength at 7 days}}$$

Breaking strength at 7 days
$$+ \frac{10{,}000 \text{ lbs.}}{\text{Breaking strength at 7 days}}$$

The *setting time* of cement is useful in aiding choice of a cement for a given class of work. Three distinct graduations of time of setting are arranged for, designated as : 'quick,' 'medium' and 'slow,' ranging from 10 minutes to 7 hours.

Finally, the *soundness* of cement, that is, its constancy of volume when set and consequent freedom from tendency to expand in the work of which it forms part, and thus to subject the work to internal stresses sometimes so great as to cause its destruction, can be determined by observing the alteration of volume and condition of test pieces made of the cement and kept under conditions designed to develop and accelerate any latent tendency of the kind. The test is carried out by means of the Le Chatelier apparatus, which consists of a small split cylinder of spring brass or other suitable metal forming a mould 30 mm. diameter and 30 mm. high. On either side of the split is attached an indicator 150 mm. long with pointed end. The mould is filled with neat cement gauged in the usual manner and placed under cold water for 24 hours. It is then boiled in water for 6 hours ;

any alteration in the distance between the points is an indication of the constancy of volume of the cement. The expansion should not exceed 10 mm. when the sample has been aerated for 24 hours, or 5 mm. after the sample has been aerated for 7 days.

The specifications in use on the Continent and in America are similar to the British Standard specification as regards their aim, which is to ensure that the cement shall be mechanically strong and chemically stable. The tests themselves are also generally similar, the chief differences concerning the use of compressive as well as tensile tests and variations in the mode of determining the soundness of the cement.

Other cements of the Portland class. Roughly it may be said that all cements made by burning a mixture of calcareous and argillaceous materials are of the Portland cement class, although they may not be true Portland cement. Roman cement is an example. It was manufactured before the invention of Portland cement by calcining the nodules of indurated chalk and clay called *septaria*, found in the Isle of Wight, and dredged upon the Kent and Essex coasts. On burning, without any preparation, these nodules give a cement having a composition of which the following analysis is an example :—

	Per cent.
Silica (SiO₂)	. . . 19·62
Insoluble residue .	5·86
Alumina (Al₂O₃)	. 10·30
Ferric oxide (Fe₂O₃)	. 7·44
Manganese oxide (MnO)	. 1·57
Lime (CaO) .	. . 44·54
Magnesia (MgO) .	. 2·92
Sulphuric anhydride (SO₃)	. 2·61
Carbonic anhydride (CO₂)	. 3·43
Water (H₂O) .	. . 0·25
Alkalis and loss .	. . 1·46
	100·00

Roman cement has been almost wholly replaced by Portland cement. It is reddish in colour and very quick-setting, this property making it useful for work which has to be exposed to water immediately after it is laid.

Various marls contain chalk and clay in about the proportion necessary to constitute Portland cement. These are burnt without preparation and form what is known as ' natural cement.' Cement of this sort is, of course, irregular in composition and is apt to be unsound. If well slaked before use, it is a serviceable material of its class. Magnesian limestones containing argillaceous matter, are largely used in the United States for making natural cement. The following is an example of their composition :—

	Per cent.
Silica (SiO°)	. . . 22·77
Alumina+Ferric oxide (Al₂O₃+Fe₂O₃)	. 10·43
Lime (CaO)	. . . 34·54
Magnesia (MgO) .	. . 21·85
Sulphuric anhydride (SO₃)	. . 1·44
Carbonic anhydride (CO₂)	. . 2·84
Alkalis	. 3·63
Water and loss . . .	. 2·50
	100·00

Hydraulic limes are cements of the Portland class, and are made by burning limestones containing sufficient clayey matter to yield the calcium silicates and aluminates necessary in hydraulic cement. There are two types, with many gradations between them. The first is Chaux de Teil, made by burning a limestone containing silica so finely divided and so evenly distributed that it unites almost completely with the lime without the aid of any considerable quantity of fluxing constituents, such as alumina and oxide of iron. Its composition is shown below :

	Per cent.
Insoluble residue	. . . 0·62
Silica (SiO₂)	. . 22·10
Alumina (Al₂O₃)	. ⎫
Ferric oxide (Fe₂O₃)	. ⎬ 1·82
	⎭
Lime (CaO)	. . . 66·72
Magnesia (MgO) .	. . 1·17
Sulphuric anhydride (SO₃)	. 0·49
Carbonic anhydride (CO₂)	. 0 64
Water (H₂O)	. . . 5·36
Alkalis and loss .	. . 1·08
	100 00

The second instance is afforded by the hydraulic lime prepared from blue lias limestone occurring in the Rugby district, near Lyme Regis and by Aberthaw In this material, the proportion of alumina is much higher relatively to the silica than in the case of the Chaux de Teil An example of its composition is appended :

	Per cent.
Insoluble residue .	. . 2·39
Combined silica (SiO₂)	. 14·17
Alumina (Al₂O₃)	. 6·79
Ferric oxide (Fe₂O₃)	. . 2·34
Lime (CaO) .	. . 63·43
Magnesia (MgO) .	. . 1·54
Sulphuric anhydride (SO₄)	. 1·63
Carbonic anhydride (CO₂)	. . 3·64
Water (H₂O) .	. . 2·69
Alkalis and loss .	. . 1·38
	100·00

As it is not designed in the case of hydraulic limes to cause complete union of the acid and basic oxides, they invariably contain free lime which needs to be slaked. This is done systematically by the manufacturer of lime of the Chaux de Teil class, but is not generally practised in this country, the operation being performed by the user. In either case, perfect slaking is necessary because any negligence in this respect will lead to expansion in the work of which the lime forms part, and the slaking must be accomplished in such a way that, whilst the free lime is slaked, the cementitious compounds remain untouched.

Cements made from blast-furnace slag. Blast-furnace slag granulated by being run into water is feebly hydraulic if its lime content is sufficiently high. It is used as a puzzuolana (*see* below). If the slag is mixed with limestone so as to bring its composition within the limits indicated for Portland cement, and the mixture is burnt, a product is obtained which is as much Portland cement as if it had been made from

chalk and clay. There is, however, a material made in Germany and known as Eisen-Portland cement, which consists of Portland cement (often made from blast furnace slag) to which some 25 p.c. of slag has been added after the manufacture of the Portland cement itself. The slag added has a puzzuolanic function similar to that of other silicious materials which are sometimes added to Portland cement. But apart from these uses of slag, various patented products, of which Passow cement and Collos cement are examples, prepared by treating liquid blast furnace slag in such a way that it becomes definitely hydraulic and will set and resist the action of water as does Portland cement, are manufactured. Processes for making these cements generally consist in suddenly cooling the liquid slag and in adding to it, at the moment of cooling, small quantities of some extraneous material such as salts of magnesium or the alkalis. The cause of the action of the mode of cooling and of the addition is obscure, but the fact remains that in this manner blast-furnace slag, which untreated is relatively inert, is converted into a true hydraulic cement.

Puzzuolanic cements. Except for limes which, being made from a silicious limestone, happened to possess hydraulic properties, the earliest kind of hydraulic cement was made from ordinary lime mixed with a puzzuolana, that is, a silicious material sufficiently active to combine with the lime and form a cementitious silicate. Natural puzzuolanas are volcanic in origin, the deposits known as Roman and Neapolitan puzzuolana, santorin earth, and trass being examples.

Analyses are given below of Roman and Neapolitan puzzuolanas and of a similar material from Java:

	Neapolitan puzzuolana	Roman puzzuolana	Java trass
	p c	p c.	p.c
Insoluble silicious matter .	35 38	25 91	50 40
Soluble silica (SiO₂) .	27 80	32 64	19 32
Alumina+Ferric oxide Al₂O₃ +Fe₂O₃	19 80	22 74	16 96
Lime (CaO) .	5 68	4 06	nil
Magnesia (MgO) . .	0 35	1 37	0 13
Sulphuric anhydride (SO₃) .	trace	trace	-
Water+carbonic anhydride (H₂O+CO₂) . .	4 27	8 92	7 57
Moisture, alkalis, loss .	6 72	4 33	5 62
	100 00	100·00	100 00

Granulated blast-furnace slag, broken brick and burnt clay are artificial puzzuolanas sometimes used to produce hydraulic cements when added to ordinary lime. The quantity to be added can be calculated on the assumption that the liberated lime combines in about the same proportion with the active silica in these as it does with the silica in Portland cement, it being understood that the silicious material is sufficiently finely ground to unite with the lime. In practice, puzzuolanic materials are usually coarsely ground, and only a fraction of the active silica enters into combination, the balance of the puzzuolana acting merely as an aggregate.

From what has been said concerning the constitution of Portland cement and the forma-

tion of slaked lime by its hydration in setting, it will be seen that there is a considerable quantity of calcium hydroxide unprovided for by any acid oxide. It follows that this will act in the same way as ordinary slaked lime in combining with any active silicious substance, and hence that puzzuolanas can be employed as additions to Portland cement which are useful in increasing its content of cementitious matter.

Use of Portland cement. The original object of manufacturing Portland cement and similar substances was to obtain a material which would both set and would resist the action of water. But it was soon found that the great mechanical strength of Portland cement made its use advantageous, even when it had not to be exposed to water, and at the present day it is the structural cement *par excellence*, and on account of the great decrease in cost due to modern method of manufacture, it tends to displace all other building cements, including common lime. Its largest application is to form concrete by cementing together any cheap inert stony material which may be locally available, and by the use of this substance, huge works of all kinds are constructed at a cost much inferior to that of the same work in masonry. It has been found that Portland cement, when made into mortar or concrete, will adhere strongly to iron and steel if the latter is clean and not too smooth, and on this observation the preparation of the material known as reinforced concrete is based. It is made by constructing a skeleton of mild steel rods, often tied together by steel wire and filled in with Portland cement concrete, the steel being so disposed as to take the tensile stresses in the composite structure. It fortunately happens that the coefficients of expansion by heat of ordinary mild steel and of concrete are nearly identical, and thus internal stresses, such as might occur where two diverse materials are bonded together and exposed to fluctuations of temperature, are of very moderate magnitude and do not appreciably influence the mechanical stability of the product. Although on the whole a permanent material, Portland cement may be injured or destroyed under various conditions incidental to its use. Set cement is the product of the action of water, but it is not indifferent to the further action of water. The products of the hydration of Portland cement and its congeners are calcium hydroxide, which is soluble in, and hydrated calcium silicates and aluminates which are decomposable by water. Therefore when water has free access to set cement and can flow through the concrete or mortar of which it forms part, the cement is dissolved and destroyed. In practice good concrete is made so nearly impermeable that, except under heavy pressure, no such flow occurs, but if the concrete is loose in texture and the flow of water correspondingly easy, destruction is only a matter of time. When the water contains salts of magnesium or calcium sulphate, which act on the lime in the one case and on the calcium aluminate in the other, forming part of the set cement, the rate of destruction is much increased. Thus it comes about that in all under-water work, and more particularly in sea water, the concrete to be permanent must be impervious. There are minor and local causes

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of destruction such as contact with waters containing dissolved gases, e.g. CO_2 and SO_2, competent to act on the calcareous constituents of cement, but in general the failure of a concrete structure, when due to chemical action and not to mechanical weakness, can be traced to the flow of water, and usually saline water, through the fabric.   B. B.

CEMENTATION v. IRON.

CEMENT COPPER v. COPPER.

CEMENT STEEL v. IRON.

CEMENTITE, an iron carbide, Fe_3C, containing 6·9 p.c. carbon, is an important constituent of cast iron and steel (Abel and Deering, Proc. Inst. Mech. Engineers, 1885, 30'; Moissan, Compt. rend. 122, 421). In steels containing 1·5 p.c. or more of carbon, free cementite is found crystallised in large pseudo-hexagonal plates (Groth, Chem. Krystallographie, 1906, 1), and in practically all steels it exists with pure iron (ferrite), in the eutectic mixture called *pearlite* (Ledebur, Stahl u. Eisen, 1898, 742).

It is very brittle and harder than hardened steel or glass (H. =6) (Müller, Stahl u. Eisen, 1898, 292), and its presence is the cause of the hardness of 'white' or 'chilled' cast iron. (Howe, Metallographist, 1901, 177). It is recognised under the microscope by its hardness and resistance to etching.

As *cohenite*, it is present in meteorites (Weinschenk, Ann. Museum, Wien, 1889, 4, 94).

CEPHAELINE v. IPECACUANHA.

CERADIA v. OLEO-RESINS.

CERARGYRITE or **Hornsilver.** Native silver haloids, $Ag(Cl,Br,I)$, occurring as small holohedral-cubic crystals and as compact masses with a horny appearance and texture. The material is soft (H. =2½), tough, and sectile, and cuts like horn. On exposure to light, it quickly darkens. The name 'hornsilber' was used by C. Gesner in 1565, and the Greek form cerargyrite was first used by F. S. Beudant in 1832. After the recognition of the bromide and chlorobromide in 1841 and 1842, the name cerargyrite came to be applied more especially to the chloride. But as the different members of the group so closely resemble one another that they can often only be distinguished by analysis, it is more expedient to include them as sub-species under the name cerargyrite (*see* Prior and Spencer, Mineralog. Mag. 1902, xiii, 174), viz. :

Chlorargyrite, AgCl.	Grey or colourless, sp.gr. 5·556.
Bromargyrite, AgBr.	Greenish-grey.
Embolite, Ag(Cl,Br):	Greenish-grey.
Iodembolite, Ag(Cl,Br,I).	Greenish-yellow to orange-yellow.

Isomorphous mixtures are the rule, and of these sub-species embolite (q.v.), with chlorine and bromine in indefinite proportions, is the most abundant. Large quantities of these minerals have been mined as silver ores in Mexico, Chañarcillo in Chile, and Broken Hill in New South Wales. They occur in the upper oxidised zones of veins of silver ore, and have no doubt been formed by the action of salt waters percolating from above.

Silver iodide forms a distinct mineral (v. IODYRITE) crystallising in the hexagonal system, but at a temperature of 146° it passes over into a cubic modification.   L. J. S.

CERASIN v. GUMS.

CERASINE, -ORANGE, -RED, v. AZO-COLOURING MATTERS. ·

CEREALS. The cereals are the fruits or seeds of various species of Gramineæ. In all parts of the world they constitute the most important food of mankind, and are utilised not only for bread and corn and the feeding of stock, but also for the fabrication of a number of fermented drinks and industrial products like starch.

The most widely distributed cereals are wheat and barley, which grow in almost all climates ; oats are more confined to northern latitudes , maize, and still more so rice, do not ripen, as a rule, north of 45° ; while the millets, sorghum, and durra are truly tropical or subtropical in their habits.

In view of their importance as food, a very large number of analyses have been made of the various cereals grown under all conditions, and of the products manufactured from them ; the most complete sources of information on this point are König, Chemie der menschlichen Nahr- und Genussm. 1903, and the various publications of the U. S. Dep. of Agric , Div. of Chemistry, particularly Bull. 13 (1899), 9, 45, and 50.

While each cereal grain possesses its own characteristic composition, subject to variations determined by climate, season, variety, &c., they have still a general similarity and possess many features in common. The predominant constituent is always starch, which, together with certain closely allied carbohydrates—the amylans—and a little sugar, forms from 50 to 80 p c of the whole grain Various proteins are also present in inverse ratio to the carbohydrates ; they fall as low as 6 p.c in rice, and rise to 20 p.c. in some varieties of wheat. A small quantity of fat or oil is also found, most abundantly in maize and oats, where the average percentage is about 5–6. The proportion of fibre and of ash varies very greatly according to whether the grain of commerce consists of the naked fruit alone, as in wheat, rye, and maize, or whether, as in barley and oats, the flowering glumes remain adherent and can only be removed by subsequent manufacturing processes. The ash of the cereal grains shows certain marked characteristics : it is always very rich in phosphoric acid, up to nearly one-half of the ash when the grain is naked ; potash and magnesia predominate among the bases, lime and soda being present in but small amounts, while still less chlorine or sulphuric acid (derived from organic sulphur compounds) are to be found ; silica is almost absent from the naked grains, but may constitute 5–20 p.c. of the ash of these grains possessing an adherent husk.

The structure of all cereal grains shows the following features in common : in addition to the chaffy membranes of the flower, which may or may not be adherent, the grain proper possesses several fibrous coats or skins. Within these skins at the end of the grain formerly attached to the plant, lies the embryo or germ, constituting about 3 p.c. of the whole, but the greater part of the seed is occupied by the starchy endosperm, the outer membrane of the embryo which abuts against the endosperm being known as the scutellum. The endosperm

consists of a series of thin-walled cells tightly packed with starch grains enclosed within a thin network of protein, but immediately below the skin there exists a row of differently shaped cells known as the aleurone layer, especially rich in protein. It will now be convenient to consider the cereals separately.

Wheat. The average composition of wheat from various sources is given in Table I., extracted from the sources above quoted. A number of other analyses may also be found in

Vilmorin, Bull. Soc. Nat. Agr. France, 1901, 61, 73.

The composition of wheat is subject to considerable variation, and as the value of the wheat for bread-making is intimately connected with the amount of nitrogen it contains, the effect of external conditions upon this constituent has been extensively studied. As factors bringing about variation, we may enumerate (1) variety, (2) climate, (3) season, (4) soil, (5) manuring, (6) date of cutting, &c.

TABLE I.—ANALYSES OF WHEAT.

	No. of samples	Water	Protein	Fat	Carbo-hydrates	Crude fibre	Ash
English	22	13·37	10·99	1·86	69·21	2·90	1·67
United States . .	168	10·62	12·23	1·77	71·18	2·36	1·82
,, ,, New York .	8	10·38	12·34	1·92	71·63	2·07	1·67
,, ,, Oregon .	11	11·53	9·19	1·72	73·61	2·25	1·69
,, ,, South Dakota	8	9·02	14·89	2·04	69·89	2·49	1·70
Canadian North-West (Fife).	18	12·05	13·84	1·79	68·53	2·21	1·58
France	70	15·20	12·64	1·41	68·92	2·00	1·66
Germany, S. and S.-W. winter wheat	52	13·37	12·29	1·71	67·96	2·82	1·85
,, ,, spring ,,	30	13·37	14·95	1·56	67·93		2·19
Russian, spring wheat .	39	13·37	17·65	1·58	65·74	—	1·66
Argentine . . .	5	9·55	12·78	1·84	71·15	2·69	1·99
American—durum . .	2	10·40	15·68	2·49	76·74	2·61	1·90
,, —einkorn . .	4	8·34	14·67	2·19	55·67	13·56	5·57
,, —emmer . .	25	8·68	13·24	1·89	60·85	11·27	4·07

(1) High nitrogen content in wheat is usually associated with a horny translucent grain, hardness, and strength (i e capacity to make a large well-piled loaf). These qualities are most markedly seen in the wheats from Manitoba, Kansas, Hungary, and South Russia, where the high nitrogen content is mainly due to environment but partly to the varieties grown. In England, where the climate tends to produce a soft, starchy wheat, it is found that variety is the chief factor in determining the proportion of nitrogen. In the typical English wheats, the variations in the percentage of nitrogen are small, 1·6 to 2·5 p c., according to the season, but certain wheats, like Rough Chaff, Red Lammas and Golden Drop, always show higher percentages of nitrogen than others like Rivett, Square Head's Master, and Stand Up, when grown alongside on the same soil and in the same season. Moreover, a few varieties have been found, notably Fife, a wheat of Galician origin but widely disseminated in Canada and the United States, which retains in England something of the high nitrogen content and strength characteristic of North-Western America, and nearly always shows a nitrogen content of well over 2 p.c. (see Hall, J. Board Agric. 1904, 11, 321 ; Humphries and Biffen, J. Agric. Sci. 1907, 2, 1 ; papers read at the Winnipeg meeting of the British Association, Jour. Board Agric. 17, 1910). Moreover, Biffen (J. Agric. Sci. 3, 1909, 86) has shown that high and low nitrogen content are Mendelian characters which segregate and are inherited without blending.

Certain new varieties thus raised, e.g. Burgoyne's Fife and Yeoman, combining the high nitrogen content and strength of Fife with

the cropping powers of English wheats, are now grown on a commercial scale.

(2) Climate is more potent than any other factor in causing variations in the composition of wheat. Leclerc and Leavett (U.S. Dep. of Agric. Div. of Chem. Bull. 128, 1910) grew the same varieties of wheat in three localities with widely differing climates, and in the next year grew on seed from each locality at all three places, with the following results as regards protein content :—

Year	Origin of seed	Protein in seed	Protein in product grown in		
			Kansas	California	Texas
1906	Kansas	16·22	19·13	10·38	12·18
1907	Kansas	19·13	22·23	11·00	16·97
1907	California	10·38	22·23	11·33	18·22
1907	Texas	12·18	22·81	11·37	18·21

Thus the seed of Kansas origin and containing 19·13 p.c. of protein, when grown in California in 1907 yielded grain only containing 11·00 p.c. of protein ; whereas in the same year seed from the same original stock but grown in California in 1906 and only containing 10·38 p.c. protein, when moved back to Kansas, yielded grain containing 22·23 p.c. of protein. In these cases, the influence of environment is enormous, and in the main the strong high nitrogenous horny wheats of the American North-West, Hungary and Russia, owe these qualities to their environment. They are spring sown when the severe winter is over ; they receive considerable rainfall during their early growing months, followed by great heat with progressive dryness of

the atmosphere, the cycle of growth being completed in four months or less. The soft low-nitrogenous wheats are generally winter sown with an equably distributed rainfall, as in Western Europe, though, as the experience of California, Oregon, Australia, and India shows, great heat and dryness at the ripening stage will not ensure a high nitrogen content. While climates like Kansas impart a high nitrogen content to all varieties, some varieties commonly grown there, like Fife, possess a high nitrogen content congenitally and retain it in climates like the English, where other wheats with a high nitrogen content in Kansas at once deteriorate.

(3) Season has a much greater effect than manuring in altering the composition of wheat, change of season being, in this respect, comparable to change of climate and environment. The variations of English seasons, however, are never sufficient to induce 'strength' comparable to that found in the wheats of the American North-West, &c.

The following table shows the variation in the composition of wheat grown on the experimental plots at Rothamsted in 1852, a wet cool year, and 1863, a dry and hot year.

(4) Taken by itself, soil has not a very large effect upon the character of the wheat grown ; in fact, in practice it is difficult to disengage the variations due to soil from those depending on the changed environment generally, soil being, as it were, a factor in climate.

(5) The composition of wheat shows some variation with the character of the manuring, but the variations are not large. The following results were obtained with the wheat grown on the Rothamsted Experimental plots in 1893, the fortieth season in which the plots had been

		2	3	7	10	11
		Dung	Un-manured	N P_2O_5 K_2O	N only	N P_2O_5
Weight per bushel, lb.	1852	58·20	56·60	56·00	55·90	55·60
	1863	63·10	62·70	62·60	62·60	62·50
Weight of 100 grains, grams	1852	3·46	2 88	3·08	3·26	2·94
	1863	5·35	5·02	4·79	4·51	4·76
Grain to 100 straw	1852	49 60	53 90	41 90	47·30	47·80
	1863	67 50	70·40	59·40	74 30	70·40
Nitrogen in dry grain, p.c.	1852	2·02	2·08	2·29	2·48	1·95
	1863	1·52	1·65	1·53	1·70	1·79
Nitrogen in dry straw, p.c.	1852	0·46	0·57	0·87	0·89	0·46
	1863	0 25	0 33	0·36	0·35	0·44
Ash in dry grain, p.c.	1852	1·98	2 03	1·95	1·83	1·96
	1863	1 85	1 95	1·73	1·56	1·72
Ash in dry straw, p.c.	1852	7·04	7·04	5·55	5·60	6·10
	1863	6·42	7·12	5·22	5·40	5·48

growing wheat with the same manures on the same land, thus setting up much more extreme differences than would occur in practice :—

Plot	Manuring	Weight per bushel lbs.	Nitrogen, p.c.	Ash, p.c.
3	Unmanured	62·7	1·997	1·84
5	Mineral, no N	62 3	2·015	2·04
6	Minerals +43lbs.N	63 1	2·187	1 98
7	,, +86lbs.N	62·5	2·401	1·92
8	,, +129lbs.N	62·4	2 352	1·89
10	86 lbs. N only	59·1	2·084	1·70
2	Farmyard manure	63·4	2·264	1·96

The wheats from these plots have also been ground and the flours resulting baked separately, whereupon they show extreme differences in quality and in the character of the loaf they yield (see Hall, l.c.).

(6) It will be seen from the table of composition that spring wheat possesses a higher nitrogen content than winter wheat, and it has been supposed that the difference can be correlated with the shorter period of growth of the former. Direct experiment, however, with the same variety of wheat sown at monthly intervals, did not support this view (Humphreys, l.c.). In the climates producing high nitrogen content and strength, the wheats must be necessarily spring sown, i.e. spring sowing and high nitrogen content are both results due to the same environment and are not casually related.

Similarly, the farmer's idea that early cutting gives rise to strength is not confirmed by experiment, though wheat cut green may appear somewhat horny. Again, premature ripening is associated with climates producing strength, though it is not the cause of strength.

(7) Various investigations have been made into the change of composition of the grain of wheat during its development (Pierre, Mem. Soc. Linnéene de Normandie, xv. 1869, 1, 220 ; Déherain, Ann. Agron. 8, 1882, 23 ; 20, 1894, 561 ; Adorjan, J. für Landw. 1902, 50, 193 ; Teller, Arkansas Expt. Sta. Bull. 52, 1899).

Hall and Brenchley (J. Agric. Sci. 1909, 3,195) obtained the results on wheat grown at Rothamsted, shown in table on opposite page.

It will be seen that the immature grain is richer in nitrogen and ash ; it also contains more ready-formed sugar, and possesses a slightly higher diastatic power. Other determinations show that in the early stages about three quarters, but at ripeness practically the whole, of the nitrogen is in the protein form. The figures, however, do not support the idea that in the later stages of filling the grain, only starch

BROADBALK, PLOT 3.—1907.

Date		Green weight of 1000 grains	Dry weight of 1000 grains	Specific gravity	Per cent nitrogen in dry matter	Per cent. ash in dry matter	Per cent. P_2O_5 in ash	Per cent. dextrose in dry matter	Maltose produced by 100 of dry matter
		Grams	Grams						
July 16	.	13·75	3·51	1·116	2·679	3·70	33·66	—	—
„ 19	.	21·05	5·43	1·116	2·406	3·03	36·91	14·99	339·4
„ 22	.	32·47	8·14	1·113	2·458	3·14	36·88	11·08	324·7
„ 25	.	39·70	11·16	1·116	2·167	2·80	38·73	7·36	541·4
„ 28	.	45·95	14·05	1·099	2·119	2·66	38·86	6·71	650·7
„ 31	.	51·30	17 99	1 116	2·055	2 39	38·68	6·23	597·1
Aug. 3	.	56·69	21 15	1·128	1·856	2 38	40·35	3·70	510·6
„ 6	.	57·91	24·97	1·113	1·828	2·16	42·54	2·42	442·9
„ 9	.	62·48	28·98	1 196	1·801	2·16	44·17	2·17	412·0
„ 12	.	63·68	32·20	1·215	1·720	2·09	44 30	1·86	378·1
„ 15	.	63·19	35·09	1 218	1 856	1·89	44·06	1·46	277·9
„ 18	.	70 89	37 93	1·231	1 787	1·96	46 50	1·99	441·6
„ 21	.	66·30	38·69	1·204	1 846	1·94	46 13	1·91	343·7
„ 24	.	61·01	37 96	1·271	1·778	1·93	46 30	2·02	322·1

enters, the material entering the grain is of almost uniform composition throughout. In the final ripening process, desiccation is the most pronounced change setting in

Carbohydrates of Wheat.—The carbohydrates present in wheat grain have been examined by Stone (U S Dep. of Agric., Office of Expt. Stations, Bull. 34, 1896), who found sucrose and reducing sugars, amylins and pentosans, in addition to starch, which is the principal constituent of the endosperm. It has also been shown by Whymper (Int. Cong App. Chem. London, 1909) that the larger granules of the starch contained in the endosperm are more readily attacked by the diastase secreted during germination.

The sugars are chiefly present in the germ, and among them Schulze and Frankfurter identified raffinose (Ber. 27, 1893, 64).

Proteins.—The proteins contained in wheat, and particularly in flour, have been the subject of considerable investigation; references to Ritthausen and the other earlier workers will be found in Osborne's papers (Amer. Chem. J. 1893, 15, 392; 1894, 16, 524; Amer. J Phys. 1905, 13, 35; 1906, 17, 223; Carnegie Inst. Washington, 1907, Pub. 84), from which the following summary has been extracted :—

'The proteins of the wheat kernel are *gliadin*, insoluble in neutral aqueous solutions, but distinguished from all the others by its ready solubility in neutral 70 p.c. alcohol; *glutenin*, a protein having a similar elementary percentage composition to gliadin, soluble in very dilute acid and alkaline solutions, but insoluble in dilute alcohol or neutral aqueous solutions, and yielding a wholly different proportion of decomposition products when boiled with strong acids; *leucosin*, an albumin-like protein, freely soluble in pure water, and coagulated by heating its solution to 50°–60°; a *globulin* similar in composition and properties to many globulins found in other seeds, and one or more proteoses which are present in very small quantity. It has also been shown that the proteins obtained from the embryo of the wheat are the globulin, albumin, and proteose above mentioned, and that these form nearly all of the protein substance of this part of the

seed. It thus appears that these three proteins are contained chiefly in the embryo, and that gliadin and glutenin form nearly the whole of the proteins of the endosperm, or over 80 p.c. of the total protein matter of the seed. It is possible that a part of the albumin, globulin, and perhaps minute quantities of the proteose, are contained also in the endosperm, for these proteins are always found in flour from which, in the milling process, the embryo is very nearly completely separated. . . .

'Gluten contains the greater part of the protein matter of the seed, together with a little starch, fat, lecithin, and phytocholesterin, and possibly some carbohydrate substance or substances of as yet unknown character. These non-protein substances are probably not united with one another in the gluten, but are mechanically mixed. The quantity of starch that remains in the gluten depends on the thoroughness of the washing, while the other substances owe their presence largely to their insolubility in water. The chief constituents of the gluten are the two proteids, gliadin and glutenin, the relative proportions of which vary with the variety of wheat from which the flour is made. The character of the gluten and the commercial value of the flour depend, to a large extent, on the proportion of gliadin to glutenin.

'In the moist gluten, these proteins are present combined with about twice their weight of water, which is gradually lost on exposure to dry air or at an elevated temperature.

'The gliadin and glutenin are present as such in the seed, and are not, as was formerly supposed, derived from other protein substances through the action of an enzyme. This is shown by the fact that they may be obtained directly from the flour by the same treatment as that which yields them from the gluten, and under conditions which preclude the action of an enzyme.

'The characteristics of the different wheat constituents, the products which they yield on hydrolysis, and related questions are also considered, and the nutritive value of wheat gluten and other proteins is discussed on the basis of the kind and amount of the cleavage products which they yield on hydrolysis.

'The amount of glutaminic acid which the gluten proteins yield is far greater than that yielded by any of the other food proteins, with the exception of gliadin from rye and hordein from barley. The proteins of the legumes and nuts which are used as food yield from 15 to 20 p.c of glutaminic acid, so that the mean amount of this amino- acid from the wheat protein is nearly twice as large. The same also is true of ammonia.

'The proportion of arginine from wheat gluten is relatively small compared with that from most other seed proteins, many of which yield from 10 to 16 p.c of this base.

'The proportion of lysine is likewise small, especially compared with that obtained from the leguminous seeds. The amount of histidine, however, does not differ very greatly from that of the other seed proteins What significance these differences have in respect to the nutritive value of these different proteins must be determined by future investigation, for it has only very recently been discovered that such differences exist.'

Fat—Wheat contains about 1 5 p.c of fat, the highest proportions being found in the wheats from the Canadian North-West. It is mostly present in the germ, in which it may amount to 15 p.c. This oil easily turns rancid, and is characterised by a high iodine number (115).

Ash.—Analyses of the ash of wheat may be found in Wolff, Aschenanalysen, Berlin, 1871 and 1880 ; Lawes and Gilbert, Chem. Soc. Trans. 1884, 45, 305.

The table given below, from unpublished Rothamsted records, shows the variations induced by manuring in 1896, the forty-fourth season in which the wheat had been grown on the same plots with the same manures.

Mill products of Wheat.—An account of the various products obtained during the conversion of wheat into flour, with analyses, is contained in Part 9, Bull. 13 (1898) U S. Dep. of Agric. Div of Chem. *See also* Maurizio, Getreide Mehl u Brot. Berlin, 1903. For milling offals, *see* Cranfield, J Agric. Sci 1914, vi. 102

Baking qualities of Wheat Flour -- The earliest attempt to determine the quality of flour in a baker's sense, *i e* the power of the flour to produce a large firm loaf, consisted in estimating the weight of gluten that could be kneaded out of a given weight of flour. While this test proved to be of value in comparing flours from similar wheats or from wheats grown in the same locality, so many exceptions occurred that

BROADBALK WHEAT GRAIN—SEASON 1896

Plot	2b	3 and 4	6	8	10ab	11	12	13	14
Ash in dry matter	1 90	1·84	1 88	1·74	1 57	1·72	1 78	1 76	1·76
Nitrogen in ,,	2 115	1·835	1 849	2 101	1 94	1 931	1·949	1·875	1·954
Ferric oxide	0 67	0 84	0 81	0 76	0 98	0 735	0 755	0·744	0·695
Lime	2 40	3 30	2 70	3 00	4·91	4 63	4 00	3 21	4·23
Magnesia	10 87	10 28	10 31	10 50	10 10	9 86	9·96	9 93	10 36
Potash	31 75	33 62	33 08	33 23	34 79	32 33	32·62	33 97	32·21
Soda	0·036	0 101	0 007	0 084	0·196	0 105	0 115	0·078	0 114
Phosphoric acid	51 70	48 34	49 61	48 97	43·07	48·09	48 30	48·79	47·83
Sulphuric acid	0 89	1 52	1 26	1 28	3 38	1·49	1 39	1 22	1·49
Chlorine	0 020	0 305	0 054	0·205	0 973	0·199	0 138	0 088	0·279
Silica	0·46	0·55	0 53	0 43	0·64	0 46	0 48	0·45	0·45
Sand and charcoal	1 29	1 38	1 86	1 61	1 40	2 30	2·18	1 45	2·39

no absolute value could be attached to the test.

Estimates based on the total nitrogen in the flour proved to be subject to the same errors Measurements were then made of the gliadin, the wheat protein soluble in 70 p.c. alcohol ; Fleurent further suggested that the ratio of the gliadin to the glutenin in the gluten determined its quality ; but these methods in turn broke down under criticism (*see* Hall, *l c.*) T. B. Wood (Jour. Agric. Sci. 1908, 2, 139, 267) regards baking quality as dependent on two factors : the size of the loaf is determined by the amount of sugar contained in the flour, together with that produced in the dough by diastatic action. This determines the evolution of carbon dioxide, under the action of the yeast, both as to rate and total amount. Then the quality of the gluten, which determines how the dough will stretch into a sponge and retain the carbon dioxide, depends on its physical character, which will vary enormously according to the state of equilibrium between the colloid gluten and the salts in the water with which it is in contact Under certain conditions the gluten loses all consistency, its physical character being entirely conditioned by the surrounding liquid.

In practice millers now add malt extract to certain flours in the dough-making process, in order to increase the evolution of carbon dioxide. Soluble phosphates are also introduced whereby the elasticity and gas-retaining power of the gluten is increased. The quantities necessary depend upon the origin of the wheat, and must be determined empirically for each flour mixture (*see* Wood, The Story of a Loaf of Bread : Cambridge University Press, 1913).

Nutritive Value of Wheat.—The nutritive value of various samples of wheat has been calculated by Chamberlain (U.S. Dep. of Agric. Div. of Chem. Bull. 120, 1909) as follows :—

Variety	Water	Digestible constituents				Ash	Production value calories per 100 lbs.	Albuminoid ratio
		Protein	Fat	Carbohydrates	Crude fibre			
North-West spring	10·11	11·78	1·41	73·04	1·17	1·85	94,717	6·6
Soft winter .	10·55	9·96	1·20	75·24	1·17	2·00	94,760	7·9
Durum .	9 77	13·02	1·72	70·77	1·33	2·02	94,457	5·8

The analyses give the digestible as distinct from the total constituents of the wheat, and in the last column but one the value of the wheat for the production of energy or increased weight is expressed as calories developable from 100 lbs. of the grain, after allowance has been made for the non-digestible portions and the work consumed in the process of digestion. The last column gives the ratio of the non-nitrogenous constituents [digestible carbohydrates and fibre + digestible fat × 2·25] to the digestible proteins.

The question of the digestibility and food value of the different fractions of the wheat grain produced in commercial milling—the comparison between 'white' and 'brown,' 'standard' or 'whole meal' bread, has received greatly increased attention during the war, which forced 'war bread' upon nearly all civilised nations. Before the war wheat was milled to yield less than 70 p c. of white flour and 30 p.c. or over of offals, during the war the extraction was raised to 80 p.c. and eventually to 90 p.c. The general result of the experience goes to show that the digestibility of the included fractions is higher than had been expected from previous experiments, and that only a comparatively small fraction of the population suffers from digestive

troubles in consequence of eating bread from flour containing a marked proportion of husk. While the old conclusion that white bread is the most concentrated and digestible of all breads is confirmed, the utilisation of the wheat grain for human food increases up to the 90 p c. extraction, both as regards available energy and protein. *See* Report of the Food (War) Committee of the Royal Society, 1918. The older literature is summarised in Hamill, Local Government Board Reports on Public Health and Medical Subjects, No. 55, 1911.

Wheat Straw.—The composition of wheat straw is more variable than that of the grain : the more complete the ripening process the more thoroughly will the carbohydrates, proteins, and valuable ash constituents of the straw be transferred to the grain. The variations in the composition of the straw in response to different conditions of soil and manuring, are minimised in the grain, which the plant endeavours to make of as constant a composition as possible. The following table (Konig) gives a few typical analyses of straw, which are followed by a table of the mean composition of the ash of straw from wheat grown on the Rothamsted plots, to illustrate the variation with manuring :—

Origin	No of samples	Water	Fat	Protein	N. free extract	Crude fibre	Ash
English winter sown .	—	13·6	1 3	3 3	3 94 [1]	37 1	5·3ₓ
German ,,	—	14 3	1 2	3 0	35 9	40·8	4·85
American spring ,,	7	9 6	1 3	3·4	43 5	38·0	4·2

BROADBALK WHEAT STRAW—MIXED SAMPLES, 10 YEARS, 1882-91.

Plot	2	3	5	7	10	11	12	13	14
Ash in dry matter .	8·13	7·69	7·95	5·89	6·02	5 84	5·69	5·93	5·52
Ferric oxide . .	0·31	0·94	0·60	0·50	0·54	0 43	0·33	0 34	0·41
Lime . . .	3·64	4·38	3·49	5·68	8 36	9·14	7 71	5·38	7·70
Magnesia . .	1·51	1 51	1·41	1·76	2·29	2 25	1·92	1·53	2·46
Potash . .	18·41	13·51	16·30	25 84	13·67	9·92	14·65	23·23	14·88
Soda . . .	0 09	0·10	0 09	0·21	0·41	0·58	0·57	0 03	0·33
Phosphoric acid .	3·87	2·97	4·24	3·81	2·26	4·26	3·64	3·38	3·87
Sulphuric acid .	3·44	3·81	4 76	5·40	6 72	5 44	5 32	5·06	5·31
Chlorine . .	2·92	1·81	1·90	6 59	2·72	1·66	2·88	5·60	2·81
Carbonic acid .	2	2	2	2	1·25	trace	none	none	trace
Silica . .	64·64	67·70	65·14	49·59	60·44	65·20	61·79	54·16	61·08
Sand and charcoal .	1·41	3·78	2·27	1·93	2·23	1·52	1·62	2·36	1·81

[1] Carbohydrates.　　　[2] Not determined.

Methods of Analysis.—In the analysis of wheat, the ordinary methods employed for feeding stuffs are followed, the only special determinations required being those of gluten and gliadin.

For the determination of gluten, 20 grams of dry flour, or of the ground wheat from which the husk has been sifted, are weighed out on to a piece of bolting silk, about 8 inches square, moistened with water and kneaded up into a paste   The silk is then gathered together over the dough and kneaded in several changes of water or under a tap until no more starchy liquid flows away, being finally kneaded in the air until it ceases to lose water   The gluten will then generally form an elastic coherent mass which can be removed from the silk without loss, weighed in its wet condition, spread on a tared sheet of glass or porcelain basin, dried at 100° to a constant weight, and weighed again   The ratio between wet and dry gluten is regarded as of some importance

For gliadin, 5 grams of flour are put in a flask with 250 c.c. of 70 p.c. alcohol, and shaken in a machine for 6 hours.   The mixture is then rapidly filtered, and 100 c.c. of the solution are placed in a Kjeldahl flask.   The alcohol is distilled off and the nitrogen in the residue is determined in the usual way.   Nitrogen $\times 5.68 =$ gliadin.

Barley.   Barley generally shows a smaller protein content than wheat ; this difference is not only characteristic of the two species, but barleys are likely to have been unconsciously selected for low protein content, thus being the quality most desired by the brewer, who has always been the chief purchaser of barley   The adherent glume and pale further cause an increase in the crude fibre and ash, as compared with wheat.

The following analyses of barley are derived, 1-6 from the author, 7 from König (*l.c.*), and 8 and 9 from Wiley (*l.c.*) :—

	Number of analyses	Water	Fat	Proteins	Carbo-hydrates	Crude fibre	Ash
English Chevalier—							
1899—grown after roots .	21	16 23	1·65	9 69	66 06[1]	4 10	2·27
1899— ,, ,, wheat .	7	16·44	1 31	9 12	66 05[2]	4 64	2·44
1900—prize winners	7	16 30	1 50	7 81	68 36[3]	3·80	2·23
1900—poor quality . .	4	16 80	2 28	10 78	64 24[4]	3·82	2·08
Chili Chevalier, 1900—prize .	1	15 6	2 06	9 44	67 04[5]	3 61	2·25
Asia Minor, four-rowed—prize	2	15 3	1·86	8 75	67 47[6]	4·38	2·24
Germany, Middle and North	120	14 05	1·80	9 88	66 75	4 77	2·75
United States .	32	10·8	2 13	10 69	69·89	4·05	2·44
Canada . .	20	11·96	2·06	10 57	68·90	4·10	2·41

The composition of barley is affected by climate, environment, manuring, &c., in the same way as the composition of wheat, barley being somewhat more susceptible to change   The commercial value of barley varies also to a much greater degree ; not only are there two distinct grades—barley for malting and barley for feeding purposes, the price of the former being nearly 50 p c. higher than that of the latter, though the two kinds grade off into one another—but special prices are paid for barley of exceptional quality.

(1) Variety   The number of barley varieties is small compared with that of wheat.   The two-rowed varieties fall into two types, wide and narrow eared, and are most prized for brewing purposes   The four-rowed and six-rowed types are not so much used for brewing   Strictly comparative analytical data are lacking.

(2) The following data, drawn from the Rothamsted records, show the effect of season and manuring upon the character of the barley— in 1893, a summer of extreme heat and dryness, and 1894, a wet and cool season :—

Plot	Manuring	Yield of grain		Weight per bushel		Grain to 100 straw		Nitrogen per cent. in grain	
		1893	1894	1893	1894	1893	1894	1893	1894
		Bush.	Bush.	lb.	lb.				
10	Unmanured	8 3	10·0	55·6	51·1	71·9	70 3	1·899	1·409
40	Minerals, no N	9·9	13·1	56 1	52·1	74·3	79·2	2·011	1·467
1A	N only	11·6	10 4	55·1	50 4	85·3	67·5	2·188	1·646
2A	N, P₂O₅, no K₂O	18 1	34·9	54·0	51·9	101·0	77·0	2·129	1·600
3A	N, K₂O, no P₂O₅	16 8	17·8	55·8	51·5	85·9	73·8	2·171	1·614
4A	N, K₂O, P₂O₅	30·8	41·4	56 3	54·1	102·2	77·7	2·081	1·440

The results, as shown in the table at top of next page, also obtained at Rothamsted, show the effect of nitrogenous manuring.

These results confirm the general opinion that barley for malting purposes should not be grown on land that is in high condition, either as a result of its previous treatment or through

the recent application of nitrogenous fertilisers.

[1] Containing starch, 57·9 p.c.
[2] Starch = 54·2 p.c.
[3] Starch = 61·5 p.c.
[4] Starch = 58·0 p.c.
[5] Starch = 61·2 p.c.
[6] Starch = 62·4 p.c.

	Dressed grain. Weight per bushel lbs.	Grain to 100 straw	Offal grain to 100 dressed grain	N in dressed grain p.c.
No nitrogen	58·0	110 4	5·9	1·61
86lbs. per acre organic N	57·3	96 6	12·5	1 79
86 lbs. per acre organic N in the previous year	55·1	72 8	34 9	2·42

Composition of Barley.—(*a*) Carbohydrates Barley contains soluble sugars, which may amount to 4 p c. of the dry grain ; sucrose is the chief constituent, but dextrose is also found, and O'Sullivan has shown the presence of raffinose. The main carbohydrate present is starch, of which H. T. Brown and his colleagues found 55·5 p c. in the dry material of 10 barleys examined (Trans. Guinness Research Lab 1903, 1, 91). The same investigators (*l.c.* 1906, 2, 312) proceeded to the determination of certain water soluble pol saccharides, called by O'Sullivan amylans, which yield on acid hydrolysis a racemic acid, glucose, arabinose and xylose

They further showed that the sum of the sugars, starch, and amylans, with a little ash and soluble protein, made up the whole of the barley grain that goes into solution when the barley is extracted with boiling water and hydrolysed with malt extract. They obtained from 9·5 to 10 p.c. of amylans on the dry weight of various samples of barley examined.

In the ' grains ' not rendered soluble by diastase, there are considerable quantities of ' furfuroids ' to be found, besides cellulose and fibre.

(*b*) Osborne and Ritthausen have examined the proteins of barley, and Osborne (J. Amer. Chem Soc. 1895, 17, 539) obtained 4·5 p.c. of an insoluble protein, 4 p c of hordein soluble in dilute alcohol, 0 3 p.c. of leucosin, and 1·95 p.c. of edestin and proteose soluble in water. It has also been shown that a small proportion of the nitrogen of barley is not combined as protein.

(*c*) The ether extract of barley is found to . contain neutral fats, free fatty acids, and lecithin.

(*d*) The following analyses show the composition of the ash of barley from the Rothamsted plots in 1871 :—

BARLEY—SEASON 1871.

	1 O Unmanured		4 O Complete minerals		1 A Nitrogen only (as ammonia)		4 A Nitrogen and minerals		1 C Nitrogen only (as rapecake)		7 Farmyard dung	
	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw
Ash in dry matter	2 64	6·17	2 77	6 96	2 38	5 51	2 64	6 70	2·84	5·54	2·87	7·55
Ferric oxide	0·49	0·78	0·41	0·46	0 35	0 35	0 31	0·44	0 35	0·42	0 31	0·31
Lime	2·91	10 04	2·67	7·21	3·29	9·91	2 51	7 56	2·31	9 52	2·22	6·56
Magnesia	7·70	1·96	7·65	1·44	7 95	1 97	8·07	1·89	7·91	2·18	7 75	1·30
Potash	29 16	19 07	29 87	27 36	28·80	17 11	30·67	33·90	28·89	26 84	29·23	29·39
Soda	1·30	5·85	0 50	1·93	2·16	13 24	0·68	2 16	0 56	2·93	0·40	2·53
Phosphoric acid	34 05	3 18	35 95	4 30	30 74	1·87	35·64	3·17	36 39	5·44	36·72	3·76
Sulphuric acid	2 24	5·53	2 15	7 26	2·19	4·51	1·56	5·54	1·60	6 02	1·65	3·27
Chlorine	1 71	6 96	0 71	7·72	3·57	15·10	0 86	14·58	0 68	4·55	0·31	11·99
Silica	19·62	44·49	18·99	42·63	18 57	37·98	20 38	32 71	19·85	42·04	21·02	42·71
Sand and charcoal	1·67	3·52	1 40	2·18	2·84	1 64	0 93	2·13	1·80	1·87	0·86	1·68

Barley Products.—The chief material prepared from barley is ' pearl barley,' in which the husk and germ have been removed mechanically. This material is also sometimes ground into barley flour. Important by-products for cattle

feeding are also the ' grains ' obtained in the brewing process after the diastatic extraction of the starch contained in malt, and the malt culms or sprouts knocked off the partly germinated barley after malting. Analyses are given below:—

	Water	Fat	Proteins	Carbohydrates	Crude fibre	Ash
Pearl barley	14·9	1·0	7·6	75·1	0·6	0·8
Malt culms	11·8	2·1	28·3	42·8	12·4	7·6
Brewer's grains (wet)	75·0	2·0	5·5	12·0	4·5	1·0
,, ,, (dry)	10·0	7·0	20·0	42·0	16·0	5·0

Maize. Maize or Indian corn is a cereal grain characterised by a high proportion of carbohydrates and oil but comparatively low protein and ash. Its composition does not vary to the same degree as that of wheat or barley. The average analyses (shown on top of page 138) are derived from Wiley (U.S. Dep. of Agric. Div. of Chem. Bull. 50, 1898) and König (*l.c.*).

The only variation in composition worthy of note is that in ' sweet corn,' varieties of which are grown in America to yield immature cobs for boiling as a vegetable, the grains contain a

Source			No. of samples	Moisture	Crude fat	Proteins	Carbo-hydrates	Crude fibre	Ash
United States,	Mean	. .	—	10·75	4·25	10·00	71·75	1·75	1·50
,,	,,	Northern	—	9·98	5·11	10·64	71·32	1·41	1·54
,,	,,	Middle West	—	12·33	4·97	10 89	68·16	2·22	1·43
,,	,,	Pacific slope	—	9 78	6·40	8·14	72·13	2·07	1·48
Italy	. . .	.	—	13 13	3·84	10 26	67·72	2·88	1·95
Germany (1880) .	.	.	14	13·00	5·11	8·62	70·54	1·38	1·34
Hungary (1880) .	.	.	38	13·00	3·85	9·06	71·10	1·69	1·30

higher proportion of sugar than is normal, especially in the immature state, and also a greater amount of oil.

Maize oil is expressed in considerable quantities from the germ, which is removed in preparing meal from the grain It is a light amber-coloured tasteless oil used for salad oil, as a lubricant, and for soap making

Carbohydrates —Less than 1 p c of sugar is present in maize, the greater part being sucrose with a small amount of reducing sugar Starch is the principal carbohydrate, but a little dextrin or other gum-like body has been found, also furfuroids and pentosans up to about 5 p c

Proteins —Osborne has isolated from maize, *myosin*, *vitellin* and another unnamed *globulin*, small quantities of two albumins, and *zein*, the characteristic protein which exists in both a soluble and insoluble form. It is noteworthy that zein, on hydrolysis, yields no lysin and no tryptophan, and certain defects in the nutrition of animals fed on maize alone have been set down to the lack of these groups in the zein molecule.

Ash —The following table from Wolff's Aschenanalysen gives the average composition of the ash of maize :—

	P c. ash in dry	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2
Red German	1 30	24 33	1 50	3 16	16 00	1 88	49 36	1 00	2·77
American .	1 28	26·75	3·85	2 56	15 24	2 00	47 47	1·20	1 93
German .	1·72	25·73	—	2 03	17 35	1 51	43 80	—	4·99

Maize Products —Maize is ground into a meal, 'corn flour,' the germ and the more flinty portions of the grain being removed, and the composition of the meal is set out in the table below, in which is also given the composition of maize ' stover,' i e. the stalk, leaves, &c , without the cob

A large number of commercial products are derived from maize, especially starch and glucose ; and the manufacturing processes give rise to various by-products—maize germ meal, gluten feed, &c , used for feeding cattle, but their composition depends entirely upon the method by which they are prepared.

	Moisture	Oil	Proteins	Carbo-hydrates	Crude fibre	Ash
Corn flour : three samples . .	12 57	1 33	7 13	78·36	0·87	0·61
Maize stover	19·81	2 56	4·19	42·87	26·02	4·55

Oats. From the food point of view, oats form one of the most valuable of the cereals, being exceptionally rich in oil and protein ; it is only the adherent husk which prevents them

from being the most concentrated of all the food grains Oats show considerable variations of composition, as the following analyses indicate :—

Origin	No. of Analyses	Water	Fat	Protein	Carbo-hydrates	Crude fibre	Ash	
Middle and North German . .	103	12 11	5 30	10·82	58·23	10·25	3·29	König
French . .	196	12·11	5·46	9 52	60·47	9·18	3·26	,,
American .	22	12·11	4·96	11·26	59·35	9·33	2·99	,,
,, (World's Fair)	72	9·96	4·42	12·07	58·28	11·92	3·35	Wiley
Scotch . .	10	16·90	5·59	11·57	57·54	8·25	2·59	Aitken [1]
Oatmeal . .	16	7·30	7·20	16 10	67·50	0 90	1·90	Atwater [2]
Oatstraw (Scotch)	10	15·32	3·45	3·04	52·59	33·95	6·96	Aitken [1]

As might be expected, the composition of oats varies with variety, climate, season, and manuring, in much the same way as wheat does. Of these variations, those due to the variety of

oat are of most importance, particularly in the

[1] Trans. H. & Ag. Soc. 1901, v. 18, 292 and 293.
[2] U.S. Dep. of Agric. Office of Expt. Sta. Bull. 28, 1899.

manufacture of oatmeal. The proportion of husk to kernel is of most significance, and the individual Scotch analyses, of which the mean is given in the table above, show variations in the fibre of from 6 to 14 p.c., and in oil, the other variable constituent, of from 4 to over 8 p.c.

Wilson (Trans. H. and Ag. Soc. 1903, v. 15, 183) gives figures relating to the amount and composition of the oatmeal obtained from several varieties of oats grown on the same experimental area in Aberdeen, as follows :—

Variety	Year	Husk, p c.	Oatmeal, p c.	Oil in oatmeal, p c.	Protein in oatmeal, p.c.
Dun . . .	1901	21·98	66·21	7·68	14·37
,,	1902	21 36	64·13	7·74	15·50
Potato . .	1901	22 24	66 32	9·59	15·44
,, . .	1902	22·47	64·02	10·01	12·31
Newmarket . .	1901	21·79	66 65	4·60	14·37
,, .	1902	20 46	64 84	6·63	13·50

See also Hendrick, Trans H. and Agric. Soc. 1910, xxii. 16.

Other Cereal Grains and Products therefrom.

Of the very large number of other cereal grains consumed as food, the following are among the most important :—

	No of samples	Water	Crude fat	Cruda protein	Carbo hydrates	Crude fibre	Ash	Authority
Rye								
German . . .	63	13 37	1 84	11 52	68·88	2·55	1 94	König
American (World's Fair) .	18	10·62	1·65	12 43	71 37	2·09	1·92	Wiley
Rice								
unhulled . .	.	10 50	1·60	7·50	67·40	9·00	4 00	⎫
hulled . .	—	12 00	2 00	8 00	76 00	1 00	1 00	⎬ Wiley [1]
polished . . .	— —	12 40	0 40	7 50	78 80	0 40	0·50	⎭
Millet (Panicum miliaceum)								
unhulled . .	6	12 50	3 89	10 61	61·11	8 07	3 82	König
,, . .	34	9 00	3 25	12 83	71 50	8 84	3 58	Chamberlain
hulled . .	9	11·79	4 26	10 51	68 16	2 48	2·80	König
Sorghum saccharatum .	38	15·17	3·36	9 26	67 99	2 51	1 71	,,
,, *vulgare* . .	12	11·46	3·79	8·96	70·25	3·59	1·95	,,
Andropogon sorghum .	10	—	3·25	11 71	81 58	1·80	—	Chamberlain

Chamberlain (*l c*) has calculated the feeding value of the cereal grains of American origin as follows :—

	Production value, cal. per gram	Starch equivalent	Albuminoid ratio
Wheat . . .	2 68	88·1	6·5
Barley . . .	1·99	84·2	8·0
Oats . . .	1·70	72 0	5·8
Maize . . .	2·23	94·2	12 3
Emmer . . .	1·64	69·4	6·0
Einkorn . .	1·60	67·8	5·2
Rye . . .	2·08	88·2	6·9
Panicum miliaceum	1·84	78·1	11·5
Andropogon sorghum	2 06	87·2	10·5

The production value represents the number of calories of energy available from the gram of food, after deduction has been made for the energy in the excreta and the energy consumed in digestion processes. The starch equivalent gives the effect of 100 lbs. of these foods in the production of fat or external work in terms of lbs. of pure starch required to produce the same effect. A. D. H.

CEREBRIN *v.* **ENZYMES.**

CEREBROSE (Galactose) *v.* **CARBOHYDRATES.**

CEREDINE. Trade name for a preparation of dry powdered yeast.

CERESIN. Ceresin occurs in commerce in the form of thin round masses several inches in diameter, harder than wax, of a dazzling white appearance ; inodorous, and transparent at the edges. The fracture is somewhat similar to that of wax, but ceresin does not become plastic in warm water. The melting-point is between 75° and 80°. It is not attacked by acids, either in the cold or when heated . but by alkalis, which do not saponify a trace of it. It is entirely volatilised at a high temperature without alteration. Ceresin is apparently a paraffin ; it does not appear to be obtained from coal tar, but from Galician 'earth-wax,' *i.e.* ozokerite. It is used as a substitute for beeswax (J. Soc. Chem. Ind. 11, 372).

CERFLUORITE *v.* **YTTROCERITE.**

CERIN and **CERYL CEROTATE** *v.* **CORK ;** **WAXES.**

CERISE. A trade name for a variety of aniline red and acid magenta.

CERITE. A hydrous silicate of cerium metals. Rammelsberg's analysis (1859) showed the presence of 64·55 p c. Ce_2O_3 with 7·28 p.c. $(La,Di)_2O_3$ and approximated to the formula $2Ce_2O_3 \cdot 3SiO_2 \cdot 3H_2O$. Later analyses showed a predominance of lanthanum and didymium, suggesting the name lanthanocerite. Crystals are orthorhombic, but of rare occurrence. The mineral is usually found as reddish granular masses much resembling in appearance certain

[1] Type analyses from various data.

varieties of corundum, from which, however, it is readily distinguished by its lower hardness (H. $5\frac{1}{2}$; sp.gr. 4·9). It occurs as a bed in gneiss at Bastnäs in Sweden, and was the material in which the element cerium was first detected. L. J. S.

CERIUM. Symbol Ce. At. wt. 140·25 (H. Robinson, Proc. Roy. Soc. 1884, 37, 150; Brauner and Baték, Zeitsch. anorg. Chem. 1903, 34, 103, 207). The most abundant of the rare-earth elements. The metal has been prepared by (1) the electrolysis of the fused chloride with or without an admixture of barium or calcium chloride or alkali chloride; (2) the electrolysis of a mixture of cerium dioxide and cerium fluoride (Borders and Stocken, D. R. P. 172529; Muthmann and Weiss, Annalen, 1902, 320, 231; 1904, 331, 1; 1907, 355, 116). By the latter process, the yield corresponds with 57 p.c. of a current of 750 amperes and 7·5 volts with current densities of 9–10 amperes and 3 amperes per sq. cm. at cathode and anode respectively.

Metallic cerium has the colour and lustre of iron; its hardness is comparable with that of silver or tin; m.p. 635° (Hirsch), 623° (Muthmann and Weiss); sp.gr. of fused product of electrolysis 6·92 at 25°; sp.heat 0·05112 (20°–100°); hardness (as determined by the scleroscope), 25·9 and 9·5 for rolled and freshly cut surfaces respectively; ultimate strength (as determined in an Olsen machine, with test bars of 0·212 in. diameter), 12,900 lb. per square inch; and no elongation with a constant load at 350 lb. Cerium is paramagnetic; magnetic susceptibility, $(\kappa) + 182\cdot2.10^{-6}$ (Monatsh. 1899, 20, 369). In dry air the metal is moderately stable, but becomes superficially tarnished with yellow dioxide. The temperature of ignition in oxygen is about 150°–180° (Annalen, 1903, 325, 261). The metal is malleable and ductile, it has a fairly high latent heat of fusion and thermal conductivity. The heat of oxidation of the metal is 1740 cals. per gram, or 60,900 cals. per gram: equiv. $(\text{CeO}_2 = 243,600)$; the wire burns even more brightly than magnesium, and combines readily with the halogens. Cerium is very slightly attacked by cold water; a slow evolution of hydrogen occurs in boiling water, and the metal is tarnished black; it is readily dissolved by dilute acids, but concentrated nitric acid produces a brown deposit consisting mainly of dioxide. By heating the metal to 345° in hydrogen, cerium hydride is produced, without luminescence. At 1000° it combines with nitrogen to form the nitride; and direct combination also occurs when the metal is heated in sulphur vapour (Hirsch, Met. and Chem. Eng. 1911, 9, 540). Alloys have been prepared by melting cerium with other metals under molten sodium and potassium chlorides; the combination with aluminium, magnesium, bismuth, silicon, or zinc is attended by a generation of heat; liquid and solid cerium amalgams have also been obtained. Cerium silicide (CeSi_2) is formed by the reduction of cerium oxide with graphite and silicon. This compound is brittle and when added to cerium in such proportion that the mixture contains about 15 p.c. of silicon, forms a good pyrophoric alloy. The magnesium-cerium alloys are excellent for thermal reduction processes since—the combination of the two metals being endothermic—

more heat is developed by the oxidation of the alloy than by that of the two metals in admixture (Hirsch).

When scratched or rubbed with a steel edge, cerium emits brilliant sparks, and this property has been utilised in the preparation of gas lighters. For a description of pyrophoric cerium alloys, see Engineering and Mining Journal, 1917, p. 212; Vogel, Zeitsch. anorg. Chem. 1917, 99, 25.

Separation and purification of ceria.—Of all the rare earth oxides, ceria is most readily isolated in a pure state, and the following methods have been employed in separating this oxide from lanthana, praseodymia and neodymia:—

(1) Treatment of the hydroxides suspended in aqueous caustic alkalis with chlorine; ceric hydroxide remains undissolved, while the other hydroxides are converted into soluble chlorides and hypochlorites (Mosander, J. pr. Chem. 1842, 30, 276 : Mengel, Zeitsch. anorg. Chem. 1899, 19, 67).

(2) The mixed oxides dissolved in hot nitric acid and the solution evaporated down with ammonium nitrate until ceric ammonium nitrate separates. The double salt is crystallised from nitric acid until the oxide left on ignition has a light-yellow colour (Auer von Welsbach, Monatsh. 1884, 5, 508; Schottlander, Ber. 1892, 25, 378); or the mixed oxides are treated with four times their weight of concentrated nitric acid and gradually heated to 60°. The solution, after decantation from any insoluble matter, is evaporated to a syrupy consistency, mixed with water from 10 to 30 times the weight of the oxides taken, and 1 gram of ammonium sulphate added for each litre of solution. The liquid is boiled for a few minutes, when a pale greenish-yellow precipitate of basic ceric nitrate and sulphate is formed, which is separated and washed with a solution of a mixture of ammonium nitrate and sulphate (Wyrouboff and Verneuil, Sterba).

(3) The solution of mixed nitrates neutralised with ammonia and boiled with magnesium or sodium acetate and hydrogen peroxide whereby cerium is completely precipitated as a basic acetate (Meyer and Koss, Ber. 1902, 35, 672).

(4) The mixed ammonium double nitrates boiled with aqueous ammonium persulphate, calcium carbonate being gradually added to keep the solution neutral. The precipitate contains all the cerium as ceric nitrate and sulphate mixed with calcium sulphate (Witt and Theel, Ber. 1900, 33, 1315; cf. Meyer and Marckwald, ibid. 3003).

(5) The joint action of potassium permanganate and a basic substance (mercuric oxide, zinc oxide, magnesia, sodium carbonate, &c.) in neutral solution. The precipitate contains all the cerium as ceric hydroxide (Stolba, Ber. böhm. Ges. Wiss. 1878; Drossbach, Ber. 1896, 29, 2452; D. R. P. 143106; Meyer, Zeitsch. anorg. Chem. 1903, 37, 378).

The last of the foregoing methods is generally applicable to the mixed oxides of the rare earths, and permits of the complete separation of cerium in one operation. These processes require to be repeated before the cerium is completely freed from the last traces of lanthanum; thorium also is removed completely, only with

some difficulty. The solution of nitrate, mixed with an excess of ammonium carbonate, is treated with ammonia when the greater portion of the thorium is precipitated. To remove the remainder, anhydrous cerium sulphate is prepared and added to ice-cold water, when the pure hydrated salt separates (Wyrouboff and Verneuil, Compt. rend. 1897, 124, 1230 ; 125, 950 ; 128, 1331 ; Urbain, Ann. Chim. Phys. 1900, [7] 19, 184 ; Sterba, *ibid.*•1904, [8] 2, 193 ; Brauner, Zeitsch. anorg. Chem. 1903, 34, 103 ; Meyer, *ibid.* 37, 378 ; Orloff, Chem. Zeit. 1906, 30, 733 ; 1907, 31, 562 ; Neish, J. Amer. Chem. Soc. 1909, 31, 517).

Only a small proportion of the cerium oxide extracted from monazite is used in the mantle industry, the greater amount is employed in the manufacture of sparking alloys for cigar lighters, &c. A further quantity is used (in the form of fluoride) for impregnating arc-light carbons ; in weighting silk, in the dyeing and photographic industries, and to a slight extent in medicine.

Cerium forms several series of compounds derived from the oxides Ce_2O_3, $Ce_4O_7(?)$, CeO_2, and CeO_3.

CEROUS COMPOUNDS.

Cerium hydride $CeH_3(?)$. Cerium combines readily with hydrogen at 250°–270°, yielding a brownish-black amorphous hydride which not improbably consists to some extent of CeH_4. This product is stable in dry air at the ordinary temperature, but on heating it is converted explosively into cerium oxide and nitride (Matignon, Compt. rend. 1900, 131, 891 ; Muthmann and Kraft, Annalen, 1903, 325, 281).

Cerous fluoride $2CeF_3,H_2O$ (John, Bull. Soc. chim. 1874, [2] 21, 533), known also in the anhydrous condition, and employed in the electrolytic production of the metal (*v. supra* ; and *cf.* Brauner, Ber. 1881, 1944 ; 1882, 109, 115 ; Monatsh. 1882, 3. 1).

Cerous chloride $CeCl_3,7H_2O$ or $2CeCl_3,15H_2O$ (J. Amer. Chem. Soc. 1894, 16, 649 ; Ber. 1902, 35, 2622).

The anhydrous chloride, a fusible deliquescent crystalline mass, is obtained by the following methods :—

(1) Heating the dry oxalate or cerium dioxide in hydrogen chloride (Robinson, Proc. Roy. Soc. 1884, 37, 150).

(2) Decomposing cerium carbide with chlorine or hydrogen chloride.

(3) Reducing anhydrous cerous sulphate to sulphide by heating in hydrogen sulphide and decomposing the latter with hydrogen chloride (Ber. 1899, 32, 3413). Cerous sulphide and hydrogen bromide yield cerous bromide.

(4) The anhydrous sulphate, when heated in a current of chlorine and sulphur chloride vapour, is converted directly into cerous chloride.

The dry chloride is readily soluble in alcohol and ebullioscopic determinations of the molecular weight in this solvent gave numbers corresponding with $CeCl_3$ (Muthmann, Ber. 1898, 31, 1829).

It forms double salts with the chlorides of mercury, gold and platinum, and of certain organic bases.

Cerous bromide $CeBr_3$, and *iodide* CeI_3 are also known, as are the *bromate* $Ce(BrO_3)_3,9H_2O$, and *iodate* $Ce(IO_3)_3,2H_2O$.

Cerous hydroxide $Ce(OH)_3$, a white precipitate obtained from soluble cerous salts with ammonia or caustic soda, is stable only in absence of oxygen. Exposed to air it becomes slowly oxidised to yellow ceric hydroxide, passing through an intermediate reddish-violet stage $xCe(OH)_3 \cdot yCe(OH)_4$ (J. Amer. Chem. Soc. 1894, 18, 649).

Cerous oxide has not been isolated with certainty, since the ignition of decomposable cerous salts (nitrate, sulphate, oxalate, &c.) leads to the production of cerium dioxide. The reduction of the latter oxide with hydrogen at high temperatures gives rise to an unstable dark-blue oxide approximating in composition to Ce_4O_7.

Cerous sulphide Ce_2S_3 (*v. supra*), a reddish purple substance (Ann. Chim. Phys. 1904, [8] 2, 193), is moderately stable in air and slowly decomposed by boiling water.

Cerium nitride CeN, obtained by heating cerium in nitrogen (Annalen, 1903, 325, 261), or by passing ammonia over heated cerium carbide (Compt. rend. 1900, 131, 865), is decomposed by water, yielding cerium dioxide, ammonia and hydrogen. An explosive cerium azide is precipitated by adding sodium azide to aqueous cerous nitrate (Curtius and Darapsky, J. pr. Chem 1900, [2] 61, 408).

Cerous nitrate $Ce(NO_3)_3,6H_2O$, prepared by (1) dissolving cerium dioxide in nitric acid in the presence of a reducing agent ; (2) decomposing cerous oxalate with strong nitric acid. Deliquescent triclinic crystals. When heated strongly, pure cerous nitrate leaves a residue of pale-yellow cerium dioxide, but when praseodymium nitrate is present, the residual oxide is brown (J. Amer. Chem. Soc. 1909, 31, 517).

Cerous sulphate $Ce_2(SO_4)_3$. The anhydrous sulphate is produced by dehydrating the hydrated salt at 400°. Above 500° it decomposes, leaving a residue of dioxide. A saturated solution of the sulphate at 0° deposits the dodecahydrate $Ce_2(SO_4)_3,12H_2O$ (asbestos-like needles). Above 5° this hydrate is labile, and at higher temperatures the solution of the sulphate deposits hydrates containing 12, 9, 8, 5, and 4 molecular proportions of water. With the sulphates of ammonium, sodium, and potassium cerous sulphate forms double sulphates isomorphous with the corresponding salts of lanthanum, neodymium, and praseodymium. In moderately strong sulphuric acid, cerous sulphate gives rise to the acid sulphate $Ce(HSO_4)_3$ (Brauner and Pieck, Zeitsch. anorg. Chem. 1904, 38, 322). This acid salt has been recommended as an oxidising catalyst in the production of aniline black, 0·3 gram of cerous oxide in this form sufficing to develop the black from 6 kilos of aniline hydrochloride.

Cerous carbonate $Ce_2(CO_3)_3,5H_2O$, prismatic crystals, precipitated from solutions of cerous salts by ammonium carbonate, forms soluble crystalline double carbonates with the alkali and ammonium carbonates.

Cerous cobalticyanide $Ce_2(COC_6N_6)_2,9H_2O$. The most soluble of the rare-earth cobalticyanides in 10 p.c. hydrochloric acid (1000 pts. of saturated solution contain 10·75 parts of the salt).

Cerous oxalate $Ce_2(C_2O_4)_3,10H_2O$, crystalline white precipitate (Power and Shedden, J. Soc. Chem. Ind. 1900, 19, 636), has been used medicinally as a sedative in sickness, particularly that of pregnancy, also in chronic diarrhœa, hysteria, epilepsy, and migraine.

Cerous phenoxide has been recommended as a non-irritant disinfectant (J. Soc. Chem. Ind. 1909, 1221 ; D. R. P. 214782).

Cerous acetylacetonate $Ce(CH_3\cdot CO\cdot CH\cdot CO\cdot CH_3)_3,3H_2O$, obtained by the interaction of cerous ammonium nitrate, acetylacetone, and ammonia (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184 ; Biltz, Annalen, 1904, 331, 334).

Cerous dimethyl phosphate $Ce_2(Me_2PO_4)_6,H_2O$ white, hexagonal plates, solubility 79·6 at 25°, and about 65 at 95° (Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10).

For other cerous salts of organic acids, r Biltz, Annalen, 1904, 331, 334 ; Wolff, Zeitsch anorg. Chem. 1905, 45, 89 ; Morgan and Cahen, Chem Soc. Trans. 1907, 91, 477 ; Pharm J 1907, 78, 428 ; Rimbach and Kilian, Annalen, 1909, 368, 110 ; Pratt and James, J. Amer. Chem. Soc. 1911, 33, 1330 ; Katz and James. ibid. 1913, 35, 872 ; Erdmann and Wirth, Annalen, 1908, 361, 190 ; Rimbach and Schubert, Zeitsch physikal. Chem. 1909, 67, 183 ; Jantsch and Grunkraut, Zeitsch, anorg. Chem. 1913, 79, 305.

For complex cerium salts, r. Wyrouboff and Verneuil, Ann. Chim. Phys. 1906, [8] 9, 289 ; Barbieri, Atti R. Accad. 1908, [5] 17, 1, 540.

CERIC COMPOUNDS.

Cerium carbide CeC_2 ; microscopic crystals, sp.gr. 5·23, prepared by melting together in the electric furnace cerium dioxide (192 parts) and sugar carbon (48 parts), using a current of 300 amperes and 60 volts (Moissan, Compt. rend. 1896, 122, 357 ; 1897, 124, 1233) :

$$2CeO_2+C=Ce_2O_3+CO$$
$$Ce_2O_3+9C=2CeC_2+3CO$$
$$CeC_2=CeC_2+C$$
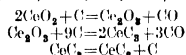
When decomposed with water, the carbide yields 75·5 p.c. acetylene, 20·5 p.c. methane, and 4 p.c. ethylene.

Cerium silicide $CeSi_2$; small crystals with a steely lustre, produced by heating cerium dioxide with crystalline silicon, stable in air and decomposed by acids (Sterba, Compt. rend. 1902, 135, 170).

Ceric oxide (*syn.* Cerium dioxide) CeO_2 ; a white or light-yellow powder, sp.gr. 6·405 ; also in isotropic crystals, sp gr. 6·76-7·905. The amorphous oxide is prepared by (1) the oxidation of the metal in oxygen ; (2) the ignition of cerous salts (nitrate, sulphate, carbonate, oxalate) or ceric compounds (hydroxide, nitrate, sulphate). The colour of ceric oxide is pure white when prepared at low temperatures, but becomes pale yellow with decrease in volume on ignition (Spencer). It ,, darkens when heated, but becomes nearly colourless or at most pale yellow when cooled. The colour of ordinary ceria is probably due to traces of praseodymium peroxide. The ignited oxide is insoluble in hydrochloric or nitric acid or in dilute sulphuric acid. The crystalline form, obtained by heating the amorphous variety with sodium chloride, borax or potassium hydrogen sulphate, is quite unaffected by acids or alkalis. The dioxide is reduced with difficulty by aluminium and magnesium, when the corresponding cerium alloys are produced. For further references to cerium dioxide, v. Compt. rend. 1895, 120, 663 ; 1897, 124, 618, 1233, 1300 ; 125, 950 ; 1901, 133, 221 ; Ber. 1900, 33, 3003, 3506 ; Ann. Chim. Phys. 1904, [8] 2, 193 ; Zeitsch. anorg. Chem. 1903, 34, 103, 207 ; 37, 378) ; Hofmann and Höschell, Ber. 1914, 47, 238 ; Jiede and Birbrauer, Zeitsch. anorg. Chem. 1914, 87, 160 ; Bekk, Ber. 1913, 46, 2574 ; Reimer, J. Amer. Chem. Soc. 1915, 37, 1636).

Ceric hydroxide $Ce(OH)_4$, a yellowish precipitate obtained from soluble ceric salts by means of ammonia or the caustic alkalis. Cerous hydroxide is slowly oxidised to ceric hydroxide by atmospheric oxygen and more rapidly by mild oxidising agents.

Although ceric hydroxide is more stable than the lower hydroxide, the ceric salts are less stable than the cerous compounds. Ceric chloride itself has not been isolated, but its additive compounds, R_4CeCl_6, with the salts of organic bases (pyridine, quinoline, triethylamine, &c.) are stable in alcoholic solution.

Colloidal ceric hydroxide is obtained by dialysing an aqueous solution of ceric ammonium nitrate. The hydrosol is readily coagulated and dries to a gummy mass, soluble in hot water (Biltz, Ber. 1902, 35, 4431 ; 1904, 37, 1095).

Ceric sulphate $Ce(SO_4)_2$ The anhydrous salt is produced by heating the dioxide with strong sulphuric acid With the diluted acid oxygen is evolved, and the resulting solution deposits, on concentration, ceri-cerous hydrogen sulphate $2Ce(SO_4)_2,Ce_2(SO_4)_3,H_2SO_4,24H_2O$ (Brauner, Zeitsch anorg. Chem. 1904, 39, 261), and then yellow hydrated ceric sulphate, $Ce(SO_4)_2,4H_2O$. The former of these compounds corresponds with the intermediate oxide $Ce_4O_7(=2CeO_2,Ce_2O_3)$.

Ceric sulphate forms a series of double sulphates (*e.g.* $Ce(SO_4)_2,2K_2SO_4,2H_2O$) with the alkali sulphates.

Basic ceric sulphates, $4CeO_2,3SO_3,12H_2O$, and $2CeO_2,3SO_3,4H_2O$ have been described by Hauser and Wirth (Zeitsch. anorg. Chem. 1908), and $CeO_2SO_3,2H_2O$, and $3CeO_2,4SO_3$ by J. F. Spencer (Chem. Soc. Trans. 1915, 107, 1265).

Ceric nitrate $Ce(NO_3)_3\cdot OH,3H_2O$. This basic salt separates from a solution of ceric hydroxide in nitric acid. The normal ceric nitrate has not been isolated, but the double nitrates $R_2^ICe(NO_3)_6$, where R^1 is ammonium or an alkali metal, are well-defined crystalline substances, having a bright-red colour ; they are very hygroscopic and readily soluble in alcohol or water. The double nitrates $R^{II}Ce(NO_3)_6,8H_2O$, where $R=Mg,Zn,Ni,Co,Mn$, form a well-defined series. These cerium double nitrates are quite analogous to the corresponding double nitrates of thorium.

For other ceric salts, *v.* Barbieri, Atti R. Accad. Lincei, 1910, [5] 16, 644 ; Ber. 1910, 43, 2214. For double ceric fluorides, *v.* Brauner, Ber. 1881, 1944 ; Monatsh. 1882, 3, 1 ; Chem. Soc. Trans. 1882, 41, 68 ; Rimbach and Kilian, Annalen, 1909, 368, 101 ; Pozzi-Escot, Compt. rend. 1913, 156, 1074 ; Browning and Flora, Amer, J. Sci. 1903 [iv.] 15, 177).

For ceric acetylacetonate, $Ce(CHAc_2)_4$, *see* Job and Goissedlt, Compt. rend. 1913, 157, 50.

Cerium peroxide and its derivatives. The addition of ammonia and hydrogen peroxide to a solution of a cerous salt determines the precipitation of reddish-brown *hydrated cerium peroxide* $Ce(O_2H)(OH)_3$. When cerous nitrate or chloride is added to concentrated aqueous potassium carbonate, the solution takes up atmospheric oxygen and assumes a deep-red colour. The liquid slowly deposits crystal-line dark-red *potassium per-ceric carbonate* $4K_2CO_3,Ce(CO_3)_3O_3,12H_2O$. In the presence of glucose, this alkaline solution acts catalytically When shaken in the air, oxygen is taken up and the per-ceric compound produced On stand-ing, this substance is reduced by the glucose to cerous salt, and the colour disappears. Re-peated shaking leads to renewed production of per-ceric compound, so that oxidation and re-duction proceed alternately to an indefinite extent (Pissarjewski, J. Russ. Phys. Chem. Soc. 1900, 32, 609; Zeitsch. anorg Chem. 1902, 31, 359; Wyrouboff and Verneul, Compt. rend. 1898, 127, 863; Job, Compt. rend. 1898, 126, 246; 1899, 128, 178, 1089; 1902, 134, 1052; 1903, 136, 45 Engler, Zeitsch anorg Chem. 1902, 29, 1; Ber. 1903, 36, 2642; 1904, 37, 49, 3268).

Applications of Cerium.—Metallic cerium (in the form of ' mischmetal,' *v.* CERIUM METALS), has been used in the reduction of the refractory oxides of columbium, tantalum, molybdenum, &c.

The oxidising action of cerium compounds has led to their use in photography (Lumière, Compt. rend 1893, 116, 574), and as oxidising catalysts in organic preparations (Atti R. Accad. Lincei, 1907 [5] 16, i. 395), and as an ingredient of ' driers.' The oxides have been suggested for use in colouring glass (Chem. Ind. 1904, 27). Cerium salts have been employed as mordants in dyeing. In the preparation of leather, hide powder decomposes cerium salts, fixing the element in the form of hydrated oxide. The hide partially reduces ceric sulphate or ceric ammonium nitrate, absorbing oxygen and yielding a good quality of leather which has a yellow tint and resists the action of water (Garelli, Atti R. Accad. Lincei, 1907, [5] 16, i. 532).

In addition to cerous oxalate, other salts (*e.g.* hypophosphate, and double ammonium citrate, tartrate and lactate) have been utilised medicinally in the treatment of sea-sickness and nervous disorders. Incandescent gas mantles contain about 1 p.c. of ceria and 99 p.c. of thoria (Meyer and Anschütz, Ber. 1907, 40, 2639).

(For the detection and estimation of cerium, *v.* ANALYSIS.)

For a bibliography of cerium, *see* Hirsch, J. Soc. Chem. Ind. 1912, 477.   G. T M.

CERIUM METALS AND EARTHS. (The Rare Earths.) The so-called rare earths include a series of basic oxides, very similar in physical and chemical properties, which are generally found associated in certain rare minerals of complex composition (silicates, phosphates, titanates, columbates, tantalates, zirconates).

The metals contained in these oxides may be divided roughly into two groups, named after the minerals *cerite* and *ytterbite*, in which the rare earths were first discovered.

The cerite metals (*cerium group*) are *cerium, lanthanum, neodymium, praseodymium* and *samarium.*

The ytterbite metals (*yttrium group*) include *dysprosium, holmium, erbium, europium, gado-linium, lutecium, celtium, scandium, terbium, thulium, ytterbium (neoytterbium),* and *yttrium.* Of the latter section, europium, gadolinium, and terbium form an intermediate series (the *terbium group*) connecting the cerium metals with the remaining rare earths of the yttrium group proper. Closely associated with these elements is the metal *thorium,* and *zirconium* is generally included in the category of the metals of the rare earths.

Historical Summary. In 1794 ytterbite, obtained from Ytterby near Stockholm, was shown by Gadolin, its discoverer, to contain a new oxide, to which Ekeberg subsequently gave the name *yttria.* From the Swedish mineral cerite, Klaproth, in 1803, isolated another new oxide which is called *ceria* by Berzelius and Hisinger, who also examined it. *Thoria* was isolated by Berzelius in 1828 from the silicate *thorite,* found at Brevig in Norway.

In 1839 Mosander isolated the oxides *lanthana* and *didymia* (Annalen, 1839, 32, 235; 1842, 44, 125) from cerite, and also effected a further separation from ytterbite of the earths *erbia* and *terbia* (Phil. Mag. 1843, 23, 251; J. pr. Chem. 1843, 30, 288). In 1878 Marignac separated from crude erbia a less basic colourless component which he called *ytterbia* (Compt. rend. 1878, 87, 578), and this fractionation was speedily followed by Nilson's discovery of *scandia,* the least basic of the ytterbite earths, and its identification as the oxide of the hypothetical *ekaboron,* predicted by Mendeléeff. In the same year Cleve effected a further separation of the old ' erbia ' and found two new earths, namely *thulia* and *holmia* (Compt. rend. 1879, 89, 478, 708). The doubt expressed by Marignac as to the homo-geneity of didymia was shared by Delafontaine, on the ground of spectroscopic evidence (Compt. rend. 1878, 87, 634), and substantiated by Lecoq de Boisbaudran (Compt. rend. 1879, 88, 323), who isolated from this earth the less basic oxide *samaria.* The didymia left after the removal of the last-mentioned oxide was still regarded as a mixture by Brauner (Monatsh. 1882, 3, 486; Chem. Soc. Trans. 1882, 43, 278), and in 1885 Auer von Welsbach, by fractional crystallisation of the double didymium nitrates of ammonium and potassium, succeeded in separating this earth into two components, which he named *neodymia* and *praseodymia* (Monatsh. 1885, 6, 477). Lecoq de Boisbaudran now showed that Cleve's *holmia* was a mixture containing a new constituent *dysprosia* (Compt. rend. 1886, 102, 1003), the simple nature of which was after-wards confirmed by Urbain (Compt. rend. 1904, 139, 736, and 1905, 141, 521).

Gadolinia, which had been recognised by Marignac in *samarskite* (Compt. rend. 1880, 90, 899), was isolated in a more definite form by Lecoq de Boisbaudran (Compt. rend. 1889, 108, 165; 1890, 111, 409, 472), and by Bettendorf (Annalen, 1890, 256, 159; 1891, 263, 164; 1892, 270, 376), and further purified by Demarçay and by Urbain and Lacombe (*v.* GADOLINIUM). Further researches by Demarçay on Cleve's samaria led to the isolation of *europia* (Compt.

rend. 1896, 122, 728), an earth provisionally symbolised as **Z**, and afterwards shown to be identical with oxides indicated by the symbols Z_ε and Z_ζ (Lecoq de Boisbaudran, Compt. rend. 1892, 114, 575; 1893, 116, 611, 674) and S_δ (Crookes, Compt. rend. 1885, 100, 1380, 1495; Proc Roy. Soc. 1885, 38, 414).

Terbia, which occurs only in small amount in ytterbite, has been isolated in a purified state by Urbain (*v.* TERBIUM), and Marignac's ytterbia (*l c.*) has been fractionated by Auer von Welsbach (Monatsh. 1906, 27, 935), and separated into two components, *neoytterbia* and *lutecia*, by Urbain (Compt. rend. 1907, 145, 759). In 1911 Urbain discovered that the lutecium from gadolinite is accompanied by a small quantity of a rare earth metal which he called *celtium* (Urbain, Compt. rend. 1911, 152, 141).

Occurrence (*v.* Das Vorkommen des seltenen Erden, Schilling, 1904; Phipson, Chem. News, 1896, 73, 145). The following is a short description of the most important sources of the rare earths :—

(For details concerning the various minerals, *see* under their respective headings.)

1. *Minerals containing chiefly Cerium Earths.*

Cerite (ochroite, cererite, cerinstein), a hydrated silicate containing 60 -70 p.c. of cerium and its allies, together with smaller amounts of iron, calcium, and the yttrium earths, found in the Bastnas mine at Ryddarhyttan in Sweden.

Orthite (allanite, bodenite, cerine, muromontite, pyrorthite, tautolite, uralorthite, wasite), a double silicate of aluminium and the cerium metals (16–25 p c.), together with smaller quantities of thorium, iron, calcium, and the yttrium metals; found in Greenland, Scandinavia (Arendal, Hitteröe, Stockholm), United States (New York, North Carolina, Pennsylvania, Virginia, Texas), Ural Mountains (Miask), and in several localities in Germany.

Monazite (cryptolite, edwarsite, eremite, mengite, turnerite), an orthophosphate of the cerium metals (Ce, La, Nd, Pr)^{III} PO$_4$, containing 40 -70 p c. of these elements together with varying amounts of thorium (0–18 p.c.); it occurs in the plutonic and older volcanic rocks, and in the alluvial sands of the rivers and coasts of Brazil, North and South Carolina, and Travancore, in the Federated Malay States, Ceylon and Nigeria, &c.

Æschenite. A complex, columbate-titanate, containing approximately equal proportions (13–23 p.c.) of thorium and the cerium metals, together with a small proportion of the yttrium group, found at Hitteröe (Norway) and Miask (Ural Mountains).

2. *Minerals containing chiefly Yttrium Earths.*

Ytterbite (gadolinite), a basic silicate containing yttrium earths (40–48 p.c.) and cerium earths (5–10 p.c.), together with glucinum and iron; found in Colorado, Germany (Harz Mountains and Silesia), Scandinavia (Fahlun, Hitteröe, Ytterby), and Texas.

Yttrialite, a silicate of the yttrium metals (43–47 p.c.), thorium (10–12 p.c.), and cerium metals (5–8 p.c.), found in Texas.

Xenotime, a phosphate of the yttrium metals

(54–64 p.c.), corresponding with monazite; it contains also smaller amounts of the cerium metals and thorium; found in Brazil, North Carolina, Georgia, Norway, Sweden and Switzerland.

The following minerals contain the yttrium earths and smaller quantities of thoria and the cerium earths united with varying proportions of the more acidic oxides of columbium, tantalum, titanium, tungsten, tin, uranium, silicon, and zirconium.

Fergusonite (bragite, kochelite), found in Ceylon, Greenland, Arendal, Ytterby, Massachusetts, North Carolina, and Texas.

Yttrotantalite, found in Norway, Sweden, and the Ural Mountains.

Samarskite (nohlite, victinghofite, ytteroilmenite), found in Canada, Connecticut, North Carolina, and Ural Mountains (Miask).

Polycrase, found in Canada, Scandinavia, and North and South Carolina.

Euxenite (loranskite), found in North Carolina, Norway Hitteröe, Brevig), and Swaziland.

Many other rare complex minerals (fluorides, zircono-silicates, titanates, columbates, tantalates, uranates, &c) contain considerable amounts of the rare earths, which are also not infrequently found in small quantities in commoner minerals (e g. limestones, apatites, scheelites, &c.) Traces of the rare earth metals have been detected in mineral waters, in the ashes of plants, in urine, and in bone ash.

Extraction of the Rare Earths.—The finely powdered mineral, made into a paste with concentrated sulphuric acid, is heated till the mass becomes dry and hard The product is extracted with water, the solution treated with hydrogen sulphide to remove copper, bismuth, molybdenum, &c., and the metals of the rare earths precipitated as oxalates by the addition of oxalic acid. The oxalates are decomposed at 400°, the residual oxides dissolved in dilute sulphuric acid, and the solution saturated with sodium or potassium sulphate, when the double sulphates of the cerium metals are precipitated, whilst those of the yttrium metals remain dissolved.

The complex minerals containing columbium, tantalum, titanium, &c., may be decomposed by hydrofluoric acid, when the foregoing elements form soluble fluorides, whilst the fluorides of the rare earth metals are precipitated. Or these minerals may be broken up by heating with strong sulphuric acid or potassium hydrogen sulphate and the rare earths precipitated by ammonia from the solution of their sulphates. These hydrated oxides are freed from the co-precipitated columbium, tantalum, and titanium hydroxides by prolonged boiling with nitric acid, when the latter hydroxides separate in an insoluble form. The rare earths are precipitated as oxalates from their solution in nitric acid, the oxalates ignited, and the resulting oxides subjected again to the nitric acid treatment until a complete separation is effected. Or the minerals may be heated in the vapour of disulphur dichloride S$_2$Cl$_2$, or carbonyl chloride COCl$_2$, when the chlorides of columbium, tantalum, titanium, &c., are volatilised, and the rare earth metals are converted into non-volatile chlorides (Hicks, J. Amer. Chem. Soc. 1911, 33,

1492; Barlot and Chauvenet, Compt. rend. 1913, 157, 1153).

The methods of separating and purifying the rare earths, which will be further described under the appropriate headings (v. CERIUM, YTTRIUM; TERBIUM; THORIUM, &c.) may be divided into the following two classes :—

1. Separations based on differences of basicity.

a. The fractional precipitation of the earths with bases of varying strengths : ammonia, caustic alkalis, magnesium hydroxide, organic bases.

b. The fractional decomposition by heat of the solid nitrates and other salts.

2. Separations based on differences of solubility.

Considerable ingenuity has been shown in separating the metals of the rare earths by taking advantage of the slight differences of solubility exhibited by their salts with acids of widely different types. The following series does not exhaust the list of compounds which have been utilised in these intricate separations : Sulphates, double sulphates, nitrates, double nitrates, chromates, bromates, formates, oxalates, succinates, ethyl-sulphates, acetyl-acetonates, dimethyl phosphates, glycollates, and sulphanilates (*cf.* James, J. Amer. Chem. Soc. 1912, 34, 757).

The progress of these separations is controlled by chemical and physical methods.

1. The chemical control consists in determining the equivalent of any fraction either by a gravimetric analysis of its sulphate (Kruss, Zeitsch. anorg. Chem. 1893, 3, 44 ; Wild, *ibid.* 1904, 38, 191 ; Brill, *ibid.* 1908, 47, 464 ; Jones, *ibid.* 1903, 36, 92 ; Brauner and Pavliček, Chem. Soc. Trans. 1902, 81, 1243), or by a volumetric analysis of its oxalate (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 202).

2. The physical methods consist in observing the magnetic susceptibility of the fractions and their spectroscope characters. The rare earths differ considerably in magnetic susceptibility, and determinations of its amount are readily made by the magnetic balance of Curie and Chereveau (Urbain, Compt. rend. 1908, 146, 406, 922 ; 1908, 147, 1286 ; 1909, 149, 37 ; 1910, 150, 913 ; 1911, 152, 141 ; 1914, 159, 323).

The most convenient spectroscopic controls are (i.) the *absorption spectra*, exhibited by solutions of the salts of many rare earths (*e.g.* neodymium, praseodymium, samarium, terbium, erbium, thulium, dysprosium and europium) ; (ii.) the *arc spectra*, in which all the rare earths give characteristic lines both in the visible and ultra-violet regions of the spectrum. Carbon electrodes are employed, the lower one containing a hollow in which is placed the salt under examination. The arc spectrum is photographed and the lines identified by comparison with the photograph of an iron spectrum taken under similar conditions. The method is extremely sensitive, although not equally so for different elements (*cf.* SPECTRUM ANALYSIS and *v.* Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904 ; and Hagenbach and Konen, Atlas der Emissionspektren der meisten Elemente, 1905). Other emission spectra (the flame, spark, and cathode luminescence spectra) have been found to give useful indications in certain cases

(Crookes, Phil. Trans. 1883, 174, [3] 891 ; Proc. Roy. Soc. 1885, 38, 414 ; 1886, 40, 77, 236, 502 : Chem. News, 1886, 54, 39, 54, 63, 76, 155 ; 55, 83, 95 ; 56, 59, 62, 72, 81 ; Chem. Soc. Trans. 1889, 55, 255 ; Proc. Roy. Soc. 1899, 65, 237 ; Lecoq de Boisbaudran, Compt. rend. 1885, 100, 1437 ; 101, 552, 588 ; 1886, 102, 153, 899 ;1536 ; 103, 113, 627 ; 1887, 105, 258, 301, 343, 784 ; 1890, 110, 24, 67 ; Bettendorf, Annalen, 1892, 270, 376 ; Baur and Marc, Ber. 1901, 34, 2460).

PHYSICAL AND CHEMICAL PROPERTIES OF THE RARE EARTHS AND THEIR MORE IMPORTANT COMPOUNDS.

Hydrides. The rare earth metals combine directly at $220°$–$270°$ with hydrogen to form brittle amorphous solids ranging in colour from bluish-black (Ce and La), indigo blue (Nd), to green (Pr), and readily dissociated at higher temperatures (Muthmann, Kraft and Beck, Annalen, 1902, 325, 261 ; 1904, 331, 581).

Oxides and hydroxides. The metals of the rare earths were formerly supposed to be diads (*cf.* Wyrouboff, Bull. Soc. chim. 1889, [3] 2, 745 ; 1899, [3] 21, 118 ; Compt. rend. 1899, 128, 1573), but they are now regarded as tervalent elements forming oxides of the type R_2O_3, although cerium, neodymium, praseodymium, and terbium are capable of yielding higher oxides. The more stable oxides of thorium and zirconium are of the form RO_2. The present view of the valency of the metals of the rare earths is supported by the following facts :—

(i.) The isomorphism of bismuth nitrate and certain nitrates of the rare earth series (Bodman, Ber. 1898, 31, 1237).

(ii.) The cryoscopic and ebullioscopic determination of the molecular weights of the chlorides and acetylacetonates (Ber. 1898, 31, 1829 ; Compt. rend 1901, 133, 289 ; Annalen, 1904, 331, 334) ; these salts are thus found to have the general formula RX_3.

(iii.) The electrical conductivity of the chlorides and sulphates in aqueous solution (Zeitsch. physikal. Chem. 1899, 30, 193 ; Amer. Chem. J. 1898, 20, 606).

(iv.) The specific heats of cerium, lanthanum and didymium (Annalen, 1873, 168, 45 ; Ber. 1881, 2821 ; Bull. Soc. chim. 1882, [2] 38, 139).

The rare earth oxides vary considerably in basic power, lanthana, praseodymia, neodymia, and ceria, Ce_2O_3, being the strongest ; whilst neoytterbia, lutecia, scandia, and cerium dioxide are among the weakest bases of the series. In general, the oxides (R_2O_3) of the cerium metals are stronger bases than those of the yttrium group.

The hydroxides are thrown out of solution as gelatinous precipitates by ammonia, ammonium sulphide, and the caustic alkalis, even in the presence of ammonium salts ; but this precipitation is prevented by citric or tartaric acid (except in the case of scandium). Unlike thorium and zirconium, the metals of the cerium, terbium, and yttrium groups are not precipitated as hydrated peroxides from neutral solutions by hydrogen peroxide, but their peroxides separate from alkaline solutions (Brauner, Ber. 1881, 14, 1944 ; Cleve, Bull. Soc. Chim. 1885, [2] 43, 53). These peroxides are very unstable, evolving oxygen at even the ordinary

L

temperature; they are completely destroyed by acids (v. CERIUM; cf. Melikoff and Pissarjewski, Zeitsch. anorg. Chem. 1899, 21, 70).

Chlorides. The chlorides of the rare earth metals are deliquescent salts readily soluble in water or alcohol, and crystallising from the former solvent with 6 or 7 molecular proportions of water. The anhydrous chlorides, which are fusible at red heat, but very slightly volatile, are obtained either by evaporating their solutions to dryness with ammonium chloride, by heating the corresponding oxides with carbon in a stream of chlorine, or preferably by heating the oxide or dry sulphate in a current of sulphur chloride or carbonyl chloride or carbon tetrachloride (Matignon and Bourion, Compt. rend. 1901, 133, 289; 1902, 134, 657, 1308, 1904, 138, 631; 1905, 140, 1181; Muthmann and Stutzel, Ber. 1899, 32, 3413; Petterson, Zeitsch anorg. Chem 1893, 4, 1; Chauveret, Compt. rend. 1911, 152, 87).

The chlorides of the rare earth metals combine additively with ammonia and organic bases (e.g. pyridine; cf. Compt rend. 1905, 140, 141; J. Amer. Chem. Soc. 1902, 24, 540; 1903, 25, 1128; Ber. 1902, 35, 2622), and exhibit a great tendency to form double salts with the less electropositive metals. The platinichlorides of the cerium metals are isomorphous and crystallise in regular octahedra (Ber. 1876, 1722, Annalen, 1878, 191, 331).

Fluorides. The rare earth metals, including thorium, are precipitated completely as gelatinous fluorides by soluble fluorides and by hydrofluoric and fluosilicic acids, in this respect differing from zirconium, which forms a soluble double fluoride.

Nitrides. The rare earth metals when heated combine directly with nitrogen to form nitrides of the type MN. They are brittle amorphous solids, decomposed by moist air or by water, forming ammonia and the corresponding hydroxide.

Nitrates. The nitrates of the rare earths dissolve readily in water or alcohol, those of the cerium group crystallising with 6 molecular proportions of water, whilst the corresponding salts of the yttrium group contain 3–6 molecules of water. The cerium metals readily furnish stable crystallisable double nitrates with the univalent and bivalent metals (ammonium, sodium, magnesium, &c.)

Sulphates. The rare earths dissolve in dilute sulphuric acid, and the solutions deposit hydrated sulphates containing frequently 4, 8, or 12 molecules of water. The octahydrated sulphates of praseodymium, neodymium, yttrium, gadolinium, and ytterbium are isomorphous (monoclinic); but the cerous salt $Ce_2(SO_4)_3$, $8H_2O$ is rhombic. With excess of acid, the normal sulphates of the rare earths are converted into acid sulphates of considerable stability (Bull. Soc. chim. 1889, [3] 2, 745; Compt. rend. 1902, 134, 657; Zeitsch. anorg. Chem. 1904, 38, 322; Chem. Soc. Trans, 1902, 81, 1243; James and Holden, J. Amer. Chem. Soc. 1913, 35, 559).

The sulphates of the rare earths have the characteristic property of combining with the **alkali sulphates**; the double sulphates of the **cerium group** are only sparingly soluble in concentrated solutions of the alkali salts, whilst those of the yttrium group are readily soluble.

The double **sulphates of the terbium group** occupy an intermediate position, being moderately soluble in solutions of alkali sulphates.

Carbides of the rare earth metals may be prepared by heating the oxides with carbon in the electric furnace. They have the general formula MC_2. They are brittle, crystalline solids, transparent in thin layers and of a yellow colour. They are decomposed by water, forming a mixture of acetylene, hydrogen, ethane, and ethylene, and the hydroxide of the metal $M(OH)_3$.

Carbonates. Ammonium, sodium, and potassium carbonates precipitate the neutral or basic carbonates from solutions of the rare earths; but these precipitates are soluble in excess of the reagents, and from the solutions thus obtained, crystalline double carbonates are deposited on evaporation. The carbonates of the yttrium metals are generally more soluble than those of the cerium group in solutions of the alkali carbonates.

Oxalates. The rare earth oxalates are precipitated by oxalic acid or soluble oxalates in neutral or acid solutions, and the sparing solubility of these compounds in acids is a characteristic property which serves to separate the rare earths from other metallic bases (Ber. 1898, 31, 1718; 1899, 32, 409).

The oxalates of the rare earths proper dissolve only slightly in ammonium oxalate, differing in this respect from the oxalates of thorium and zirconium, the latter being also soluble in free oxalic acid (Chem. Soc. Trans. 1898, 73, 951). Aqueous ammonium acetate dissolves the oxalates of the yttrium group (Bull. Soc. chim 1896, [3] 15, 338).

Formates. The formates of the cerium group are less soluble than those of the yttrium group. These salts have proved useful in separating the elements of the terbium group.

Acetates. The acetates of the cerium group are very soluble and crystallise with difficulty; those of the yttrium group are less soluble. Boiling with sodium acetate precipitates zirconium and thorium from solutions of their soluble salts, but not the rare earths proper, excepting cerium from ceric salts (Ber. 1902, 35, 672).

Acetylacetonates. Acetylacetone furnishes well-crystallised salts with the rare earths, and the fractionation of these compounds from alcohol has served in the separation of the yttrium group (Urban, Compt. rend. 1897, 124, 618; Bull. Soc. chim. 1897, [3] 17, 98; Ann. Chim. Phys. 1900, [7] 19, 184; Biltz, Annalen, 1904, 331, 60; Zeitsch. anorg. Chem. 1904, 40, 218; Hantzsch and Desch, Annalen, 1902, 323, 26; Biltz, ibid. 1904, 331, 334; James, J. Amer. Chem. Soc. 1911, 33, 1332; Morgan and Moss, Chem. Soc. Trans. 1914, 105, 189).

Dimethyl phosphates. A solution of the rare earths is made in dimethyl phosphoric acid, the temperature raised and the precipitate collected; additional fractions are obtained by evaporating the mother liquor. In the case of a material containing gadolinium with just sufficient terbium to colour the oxide orange-brown, the gadolinium collects in the most soluble fraction, and the terbium in the least soluble. Lanthanum, cerium, praseodymium, and neodymium are left in the mother liquor.

Samarium, europium, and gadolinium are much less soluble than these, but more soluble than terbium, dysprosium, and holmium, erbium thulium, yttrium, and ytterbium collect in the least soluble fractions (Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10).

The Metals of the Rare Earths.—The oxides of the rare earths are very refractory substances, which have not been reduced directly; the metals are generally set free from the anhydrous chlorides. This reduction may be effected with sodium or potassium, but is preferably carried out electrolytically. The dry chlorides, mixed with a small proportion of alkali chloride, or barium chloride, are electrolysed in a copper crucible, fitted with carbon electrodes, the electrolysis being carried out with a current of 30–40 amperes and 12–15 volts. The mixed metal collects in a molten state round the cathode, which passes through the bottom of the crucible. The anode is movable, so that the resistance and therefore the temperature can be increased until all the separated metal melts together. A yield of 750 grams of metal can be obtained with a current of 120 amperes in 6 hours.

With the mixed chlorides, prepared from the waste oxides of the thoria manufacture, the product is the so-called 'mischmetal' (Ce, 45 p c.; La, Nd, Pr, 35 p c.; Sm, Er, Gd, Y, 20 p c.), which has been used, like aluminium in the Goldschmidt process ('thermite'), to effect the reduction of the refractory oxides of molybdenum, vanadium, columbium, and tantalum (Muthmann, Hofer, and Weiss, Annalen, 1902, 320, 331; 1904, 331, 1; 1905, 337, 370).

Bibliography of the Rare Earths—Böhm, 'Darstellung der seltenen Erden; Browning, Introduction to the Rarer Elements; Abegg, Handbuch der Anorganischen Chemie, vol. iii part i; Herzfeld and Korn, Chemie der seltenen Erden; Wyrouboff and Verneuil, La Chimie des Terres Rares   G. T. M.

CEROSIE *v.* SUGAR CANE WAX AND WAXES.

CEROSILINE *v* WAXES.

CEROTENE $C_{27}H_{54}$. A crystalline hydrocarbon, m.p. 65°, found by König and Kiesow (Ber. 6, 500) associated with cholesterol in the fat wax of hay and straw, and detected by Knecht and Hibbert in ordinary household chimney soot (Mem. Manchester Phil. Soc. 1914, 58, [2] 1).

CEROTIC ACID $C_{25}H_{51}COOH$ is found free in beeswax (Brodie, Phil. Trans 1848, i 147; Marie, Ann. Chim. Phys. 1896 [7], 7, 145) and combined as ceryl cerotato in insect wax (Brodie, l.c.; Henriques, Ber. 1897, 30, 1415). though some doubt has been expressed as to the identity of the latter acid with that in beeswax.

CEROTIN *v.* WAXES.

CEROTINE-ORANGE, -PONCEAU, -SCAR-LETS, -YELLOW *v.* AZO- COLOURING MATTERS.

CEROXYLIN *v.* WAXES.

CERULEÏN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

CERUSSITE. Native lead carbonate ($PbCO_3$), of some importance as an ore of lead (Pb, 77·5 p.c.), being known as white lead-ore. It crystallises in the orthorhombic system and is isomorphous with aragonite ($CaCO_3$) and

witherite ($BaCO_3$). Six-rayed stellate groups of twinned crystals are extremely characteristic. The crystals possess an adamantine lustre, are very heavy (sp.gr. 6·5), and effervesce with dilute acid; they are very brittle, breaking with a bright conchoidal fracture; hardness, 3–3½. The mineral occurs in the upper oxidised zones of veins of lead ore, having been formed by the action of carbonated surface waters on galena. Enormous deposits of cerussite intermixed with embolite (silver chloro-bromide) and iodyrite (silver iodide) have been extensively mined at Broken Hill in New South Wales, where little or none of the oxidised ore now remains. Intimately mixed with hemimorphite (hydrated zinc silicate), it is abundant at Broken Hill in North-Western Rhodesia   At both of these localities, many finely crystallised specimens have been found   L. J. S.

CERYL ALCOHOL *v.* WAXES.

CETIACOL. Trade name for pyrocatechol methylacetyl ether.

CETINE *v.* WAXES.

CETOSAN. Trade name for a mixture of the higher alcohols of spermaceti, mainly cetyl and octodecyl alcohols, with vaseline. When shaken with water, it forms a permanent creamy emulsion (Blatz, J. Soc. Chem. Ind 1908, 865).

CETYL ALCOHOL, CETYLIC ACID and **CETYL-ACETIC ACID** (*v.* SPERMACETI).

CETYLMALONIC ACID

$$CH_3(CH_2)_{12}CH(CO_2H)_2$$
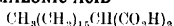
Prepared from a-cyanstearic acid and potash (Hell and Sadomsky, Ber. 1891, 2781), or diethylmalonic ester, methyl iodide, and cetyl iodide (Guthzeit, Annalen, 206, 357); m.p. 121·5° 122°.

CEVADINE AND THE ALKALOIDS OF VERATRUM SPP. The sources principally concerned are the seeds of *Schœnocaulon officinale* (A. Gray) [*Asagrœa officinalis* (Lindley)], and the rhizomes of *Veratrum viride* (Ait.) (green hellebore) and *Veratrum album* (Linn.) (white hellebore), all of which belong to the N. O. *Liliaceœ*, and have nothing in common with the hellebores proper, which belong to the N. O. *Ranunculaceœ.* The alkaloids present in these three drugs are as follows · -

Sabadilla seeds	Cevadine (crystallised veratrine)
	Cevine (sabadinine)
	Veratridine (amorphous veratrine)
	Sabadilline (cevadilline)
	Sabadine
White Hellebore	Protoveratrine
	Jervine
	Pseudojervine
	Rubijervine
	Protoveratridine
	Veratralbine
Green Hellebore	Cevadine
	Veratridine
	Jervine
	Pseudojervine
	Veratralbine

It should be noted that there has been considerable confusion in the nomenclature of these alkaloids. Commercially the name 'veratrine' is applied to an amorphous mixture of alkaloids obtained from sabadilla seeds. The name

veratrine is also frequently applied to veratridine, usually, however, with the prefix ' amorphous,' and to cevadine, with the prefix ' crystalline.' The name veratridine was also applied by Robbins (Pharm. J. 1877–1878, [iii.] 8, 316) to a crystalline alkaloid contained in green hellebore, and which, in some respects, resembles protoveratrine. It is not identical with Bosetti's veratridine isolated from sabadilla seed (Ber. 1883, 16, 1384).

Alkaloids of Sabadilla Seeds.

Cevadine (*crystallised veratrine*) $C_{32}H_{49}O_9N$ is the chief alkaloid of sabadilla or cevadilla seeds (*Schoenocaulon officinale* [A. Gray]).

Preparation. The finely-powdered seeds are extracted with alcohol, containing 1 p.c. of tartaric acid. The acid liquid is evaporated and diluted with water, to precipitate resin. To the clear solution soda is added in slight excess, and the mixture completely extracted by repeatedly shaking with ether. The ethereal solution is mixed with light petroleum and the filtrate allowed to evaporate spontaneously. Crystals of cevadine separate from the syrup, and are recrystallised from their solution in alcohol. The remaining syrup contains veratridine (amorphous veratrine) and sabadilline (Wright and Luff, Chem. Soc. Trans. 1878, 33, 338).

' Commercial veratrine ' is a macroscopically amorphous mixture of cevadine and veratridine (*q.v.*), possibly with small quantities of other alkaloids. It was deleted from the B.P. 1914, but is retained in the U.S.P. It is used externally, chiefly against lice. Sabadilla seeds contain about 0·7 p.c. of total alkaloids, of which about one-seventh can be crystallised (cevadine).

Properties. Rhombic prisms, containing $2C_2H_5OH$ when crystallised from alcohol. The alcohol is lost at 130°–140°, and the alkaloid then melts at 205° with decomposition. Nearly insoluble in water, soluble in alcohol or ether. Optically inactive (Freund and Schwarz, Ber. 1899, 32, 800).

The aurichloride, m.p. 182° (decomp.), and the mercurichloride, m.p. 172° (decomp.), are characteristic crystalline compounds (Ahrens, Ber. 1890, 23, 2700). In carbon disulphide solution additive compounds with chloral and bromal are formed (Frankforter and Kritschevsky, J. Amer. Chem. Soc. 1915, 37, 2567).

Cevadine is intensely poisonous; minute quantities cause violent sneezing.

Reactions.—When warmed with concentrated hydrochloric acid cevadine produces a fine purplish-red colour, which is a somewhat delicate test for the alkaloid. Concentrated sulphuric acid produces a carmine-red colouration, or, if the alkaloid is previously mixed with a little sugar, a blue colour.

Cevadine is a monacidic tertiary base. It contains no methoxyl groups and no : NMe group ; one HO· group is present.

When anhydrous cevadine is distilled β-picoline is obtained with tiglic acid.

When heated with alcoholic potash, cevadine undergoes hydrolysis furnishing

Cevine $C_{27}H_{43}O_8N$

and angelic and tiglic acids $C_5H_8O_2$ (Wright and

Luff, Chem. Soc. Trans. 1878, 33, 338 ; 1879, 35, 405 ; Bosetti, Arch. Pharm. 1883, [iii.] 21, 81 ; Ahrens, Ber. 1890, 23, 2700 ; Freund and collaborators, *ibid.* 1899, 32, 801 ; 1904, 37, 1964). Cevine crystallises with $3\frac{1}{2}H_2O$ from dilute alcohol, m.p. 195°–200° (anhydrous), and yields derivatives both with metals and acids. It is less toxic than cevadine (Freund, *l.c.*).

According to Hess and Mohr (Ber. 1919, 52 B, 1984) cevine is identical with *sabadinine*, which Merck (Arch. Pharm. 1891, 229, 164) isolated from the mixed alkaloids of sabadilla seeds.

Veratridine (*amorphous veratrine*) $C_{37}H_{53}O_{11}N$ is found in sabadilla seeds, and is isolated from the amorphous alkaloids precipitated in the earlier stages of the preparation of cevadine (*see* above) by treating them with ether, when they separate into insoluble matter (sabadilline) and soluble matter (veratridine). The latter is purified by conversion into the sparingly soluble nitrate. Veratridine is sternutatory, yellowish-white, amorphous, soluble in 33 parts of water, and melts at 180°. On hydrolysis by alkalis it yields *verine* $C_{28}H_{45}O_8N$, which closely resembles cevine (*see* above) and veratric acid (3 : 4 dimethoxybenzoic acid).

Sabadilline (*cevadilline*) $C_{34}H_{53}O_8N$ is a second amorphous alkaloid occurring in sabadilla seeds. It yields amorphous salts (W. and L. *l.c.*).

Sabadine $C_{29}H_{51}O_8N$, crystals, m.p. 238°–240°, also occurs in sabadilla seeds ; the salts are crystalline (Merck, Arch. Pharm. 1891, 229, 164).

Sabadilline and sabadine resemble cevadine in action, but are less toxic.

Cevadine and veratridine, the two principal alkaloids in ' commercial veratrine,' cannot be separated by crystallisation of the former from alcohol, or extraction of the latter by water, but they may be estimated by hydrolysing with alcoholic sodium hydroxide, acidifying, and estimating the volatile tiglic acid (from the cevadine), and the non-volatile veratric acid (from the veratridine) ; the latter acid is extracted by ether (Wright and Luff, *l.c.*).

Alkaloids of White Hellebore Rhizome.

Protoveratrine $C_{32}H_{51}O_{11}N$ is the characteristically toxic alkaloid of white hellebore ' roots.' It crystallises in thin four-sided tablets from alcohol, m.p. 245°–250°, 239°–241° (Bredemann), and dissolves in sulphuric acid with a green colouration, which gradually passes into deep blue. It is readily decomposed by acids yielding *iso*butyric acid as one product.

Protoveratrine is accompanied in white hellebore rhizomes by

Jervine $C_{26}H_{37}O_3N$, prismatic crystals, m.p. 238°–242° ; toxic.

Pseudojervine $C_{29}H_{43}O_7N$, six-sided tablets, m.p. 300°–307° ; not poisonous.

Rubijervine $C_{26}H_{43}O_2N$, long prisms, m.p. 240°–246°, 234° (Bredemann) ; not poisonous.

Protoveratridine $C_{24}H_{45}O_8N$, four-sided plates, m.p. 265° ; not poisonous.

The chief papers relating to protoveratrine and its congeners are Wright and Luff (Chem. Soc. Trans. 1879, 35, 405), Salzberger (Inaug. Diss. Erlangen, 1890 ; Arch. Pharm. 1890, 228, 462, the most important paper on the subject), Pehkschen (Inaug. Diss. Dorpat, 1890 ; J.

Pharm. Chim. 1890, [v.] 22, 265), and Brede-mann (Apoth. Zeit. 1906, 21, 41, 53).

Alkaloids of Green Hellebore Rhizome.

The chief alkaloids occurring in this drug (*Veratrum viride*, U.S.P.) have been described already, viz. cevadine (*see* under *Alkaloids of sabadilla seeds*), jervine, and pseudojervine (*see* under *Alkaloids of white hellebore rhizome*). Veratridine (*see* under *Alkaloids of sabadilla seeds*) occurs only in traces in green hellebore. Robbins isolated from green hellebore rhizomes (Pharm. J. 1877-1878, [iii.] 8, 316) a crystalline alkaloid which he called veratridine, and which, like protoveratrine of white hellebore, gives a green colouration with sulphuric acid. The amorphous alkaloid veratralbine was also obtained by Wright and Luff from this source (Chem. Soc. Trans. 1879, 35, 421).

CEYLON MOSS *v.* ALGÆ.

CHAGRAL GUM *v.* GUMS.

CHAILLETIA TOXICARIA (Don.). A plant found in Upper Guinea, Sierra Leone, and Senegambia, the seeds of which contain a poisonous resin used for killing rats and other animals (Power and Tutin, J. Amer. Chem. Soc. 1906, 28, 1170).

CHALCANTHITE. Native copper sulphate, $CuSO_4,7H_2O$, found as a bright-blue efflorescence, or rarely as distinct crystals, in many copper mines, being especially abundant in some of the Chilean mines. In solution it is always present in the waters issuing from copper-mines; these are allowed to flow over scrap iron, the copper being precipitated as cement-copper. About 100 tons of copper have been so saved annually from the waters of the Rio Tinto mine in Spain, and considerable amounts were formerly obtained from the mine waters in Co. Wicklow.

L. J. S.

CHALCEDONY. A native form of silica occurring in reniform, botryoidal, or stalactitic masses lining and filling cavities in rocks. It is usually greyish or creamy-yellow in colour, and has a characteristic waxy lustre with a certain degree of translucency. It possesses a minutely fibrous structure, the fibres being arranged perpendicularly to the concentric banding of the material. The optical character and orientation of the fibres is variable; and based on these differences French authors have distinguished several forms of silica under special names (quartzine, lutecite, lussatite, chalcedonite, and pseudochalcedonite). The physical characters of the mineral approach those of quartz, but with slightly lower values; sp.gr. 2·57–2·64; hardness 6½–7; n_{Na} 1·5325, 1·5435. Analyses show, in addition to silica, the presence of variable amounts of impurities (iron oxides, alumina, &c.), and on the average about 1 p.c. of water. The water is probably present as adsorbed water held between the fibres; and its presence supports the idea that the mineral was deposited in a colloidal form as hydrated silica, and that it afterwards passed into minutely crystalline quartz. Depending on the nature of the impurities present (and partly also on the state of aggregation of the material) the mineral may be of various colours, and on these differences are based several trivial varieties which are used as semiprecious stones. *Carnelian* owes its red colour

to ferric oxide, and *sard* its brown colour to hydrated ferric oxide; sard passes over into carnelian when ignited. The apple-green colour of *chrysoprase* is due to nickel silicate and the dark-green of *plasma* to an iron silicate. *Heliotrope* shows blood-red spots on a dark-green ground. Smoke-grey *flint* passes imperceptibly into more typical chalcedony. In *agate* differently coloured layers are banded together in the same stone. The uses of chalcedony are the same as those of agate (*q.v.*). On the artificial colouring of chalcedony, *v.* AGATE.

L. J. S.

CHALCOCITE *v.* COPPER-GLANCE.

CHALCOPYRITE *v.* COPPER-PYRITES.

CHALCOTRICHITE. Native cuprous oxide (*v.* CUPRITE).

CHALK. A white or greyish, loosely coherent kind of limestone rock, composed almost entirely of the calcareous remains of minute marine organisms (foraminifera, coccoliths, &c.) and fragments of shells. The purest kinds contain up to 99 p.c. of calcium carbonate in the form of the mineral calcite. Silica is always present in small amounts as the mineral opal, representing the remains of other minute marine organisms (radiolaria, &c.) and sponge spicules; and it is often segregated as the nodular masses of flint so commonly found embedded in chalk rock. Minute grains of quartz, felspar, zircon, rutile, and other minerals are also often present. With the admixture of clayey material there may be an insensible gradation from pure chalk to *chalk-marl* (*v.* MARL). In *phosphatic chalk*, there is much calcium phosphate (up to 45 p.c.); in green *glauconitic chalk* there is an admixture of grains of glauconite (a hydrated iron potassium silicate); and in *red chalk* there is some iron hydroxide. Not only may there be considerable variations in the composition of chalk, but there may also be wide variations in the colour (snow-white, grey, &c), and texture of the material. It may be soft, incoherent, and porous, or quite hard and crystalline (as the chalk of the Yorkshire coast).

The following analyses of chalk are selected from those quoted by A. J. Jukes-Browne, The Cretaceous Rocks of Britain, Mem. Geol. Survey, 1903 (which *see* for details respecting the English chalk); I, Middle Chalk from Wye, Kent; II, Chalk Rock from Boxmoor, Hertfordshire; III, soft white Upper Chalk from Farnham, Surrey:—

		I.	II.	III.
CaO	. . .	52·750	54·900	55·18
MgO	. . .	0·211	0·374	0·30
Fe_2O_3	. . .	0·067}	0·347	0·40
Al_2O_3	. . .	0·113}		
MnO	. . .	0·149	—	—
K_2O	. . .	0·098	—	0·22
Na_2O	. . .	0·013	—	0·21
CO_2	. . .	37·670	42·101	42·57
P_2O_5	. . .	0·106	0·713	0·08
SO_3	. . .	0·082	0·465	0·09
Cl .	. . .	0·006	—	—
SiO_2 (soluble)	.	0·035	0·128	—
H_2O . . } Organic matter }		5·400	—	—
Insoluble	. .	2·480	1·003	0·87
		99·180	100·031	99·92
$CaCO_3$.	. .	85·61	97·001	95·76

The uses of chalk are numerous. For example, as a writing material in form of white and coloured crayons ; for the manufacture of quicklime, mortar, Portland cement, plaster, &c., and as a fertiliser. Whiting is prepared by grinding chalk and collecting the finer sediments from water ; this is used for polishing, making putty, and many other purposes. Under the name of ' Paris white,' chalk is used in the manufacture of india-rubber goods, oilcloth, wall-paper, &c. The harder kinds are extensively used as a building stone.

Large quantities of chalk are quarried in the counties of Kent, Surrey, Sussex, Cambridge, Lincoln, and Hampshire ; Kent being by far the most important. The production of English chalk is not far short of five million tons per annum. A certain amount of this is exported to the United States, though there are extensive beds of chalk in Kansas, Arkansas, and Texas.

L. J. S.

CHALK, FRENCH. Steatite or soapstone.

CHALKONES ($\chi\alpha\lambda\chi\delta s$, an ore, particularly copper), the name proposed by v. Kostanecki and Tambor (Ber 1899, 32, 1923) for benzalacetophenone and its derivatives, on account of the fact that by suitable transformations they can be made to furnish reddish-yellow dyestuffs

In order to show the relationships of the various chalkones with one another, the following scheme of notation is adopted :—

$$3' \quad 2' \qquad\qquad 2 \quad 3$$
$$4' \bigcirc 1'-CO-CH=CH-1 \bigcirc 4$$
$$5' \quad 6' \qquad\qquad 6 \quad 5$$
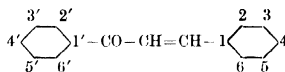
Benzalacetophenone is obtained by the action of sodium hydroxide on an alcoholic solution of benzaldehyde and acetophenone at ordinary temperature. For this purpose 21 grams benzaldehyde and 24 grams acetophenone are dissolved in 200 grams alcohol and 20 grams of a 10 p.c. solution of sodium hydroxide added. The mixture is then allowed to stand for 24 hours, and the precipitate collected and recrystallised from alcohol. Benzalacetophenone is a yellow crystalline solid which dissolves in concentrated sulphuric acid with an intense yellow colour. By heating 10 grams benzaldehyde with 30 grams acetophenone (dissolved in 100 grams alcohol) for a quarter of an hour at water bath temperature with 25 grams of a 40 p.c. solution of sodium hydroxide, *benzaldiacetophenone* $C_6H_5\cdot CH(CH_2\cdot CO\cdot C_6H_5)_2$ is obtained. This melts at 85° and crystallises in colourless prisms. Its solution in concentrated sulphuric acid is colourless, but gradually shows a blue fluorescence, and on standing for one or two days becomes faint yellow in colour, showing a strong green fluorescence. Similarly by using a mixture of 21 grams benzaldehyde with 36 grams acetophenone in 200 grams alcohol and warming with 50 grams of a 40 p.c. solution of sodium hydroxide for 12-24 hours at 40°-50°, *dibenzaltriacetophenone* is formed. It is a white crystalline solid, which melts at 198°. It dissolves slowly in concentrated sulphuric acid, the solution after some time developing a red colour and a cinnabar-red fluorescence, which slowly disappears. By carrying out the preparation at boiling water-

bath temperature, an isomeride melting at 256° is obtained (v. Kostanecki and Rossbach, Ber. 1896, 29, 1488).

Of the various derivatives, the 2'-hydroxychalkones possess the greatest importance, on account of their relationship to the naturally occurring dyestuffs of the flavone and flavanol groups ; *e.g.* chrysine, luteoline, apigenine fisetin, &c. (*q.v.*).

The 2'-hydroxychalkones are obtained by the condensation of o-hydroxyacetophenones with aromatic aldehydes in the presence of sodium hydroxide

2'-Hydroxychalkone

$$HO\cdot C_6H_4\,CO\cdot CH:CH\cdot C_6H_5$$
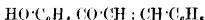
crystallises in yellow needles, melts at 88°-89°. dissolves in alkali hydroxides with an orange colour, and in concentrated sulphuric acid with a yellow colour (v. Kostanecki and Tambor, Ber 1898, 31, 715). It is converted into flavone by the action of alkali hydroxides on the dibromo-addition product of its acetyl derivative (v. Kostanecki and Feuerstein, *ibid.* 1758).
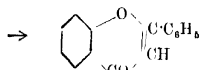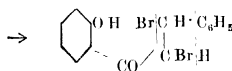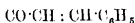
Numerous hydroxychalkones are described in the papers of v. Kostanecki and his pupils, for which consult Ber. 1898, *et seq.*

CHALMERSITE. A sulphide of copper and iron, $CuFe_2S_3$, first found as small orthorhombic crystals with pyrrhotite in the Morro Velho gold mine, Minas Geraes, Brazil. Later it was found in considerable quantity in the Ellamar district and on Knight Island in Prince of Wales Sound, Alaska, where it has been mined as an ore of copper Here the material is massive and intimately intergrown with copper-pyrites. It is pale yellow in colour with metallic lustre, and is strongly magnetic ; sp.gr. 4·68 ; hardness 3½.

L. J. S.

CHALYBITE. Native iron carbonate, $FeCO_3$, forming rhombohedral crystals isomorphous with calcite ($CaCO_3$), and of importance as an ore of iron. It is often known as siderite, but this name had earlier been applied to two other mineral species, and it is also used as a group name for meteoric irons. Sp.gr. 3·9 ; hardness, 3½. Small, brilliant crystals of varying habit are common in many mineral veins, for example, those of Cornwall. Veins of massive sparry material showing cleavage surfaces (*Spathic iron-ore*) are mined in the Brendon Hills in Somersetshire, in Weardale, Co. Durham, the Siegen district in Westphalia, dep. Isère in France, &c. The fresh, unaltered material is creamy white in colour (' white ore '), but when slightly weathered it is brown (' brown ore '). The Cleveland ore is a pisolitic form of chalybite occurring as beds in the Lias strata ;

and the important *clay-iron-stone* and *black-band iron-stone* of the Coal-measures consist of compact chalybite, intermixed with clay and carbonaceous matter. A nodular form with an internal radiated structure is known as *sphærosiderite*.

Analysis I is of pure selected crystals from near Camborne, Cornwall (A. Hutchinson, Min. Mag. 1903, xiii, 209); II-IV of ores, by A. Dick, in Iron Ores of Great Britain, Mem. Geol. Survey, 1856–1862 ; II yellowish-grey spathose ore from Weardale ; III greenish-grey earthy oolitic ore from Cleveland (also K_2O 0·27 in the portion soluble in HCl) ; IV clay-iron-stone from Shelton colliery, Hanley, Staffordshire.

	I	II	III.	IV.
FeO	61·08	49·47	39·92	46·35
Fe_2O_3	—	—	3·60	3 00
Al_2O_3	- -	trace	7·86	0 30
MnO	1·12	2 42	0·95	1·61
CaO	0 10	3·47	7·44	1·93
MgO	0·13	3·15	3 82	2·24
CO_2	38·19	37 71	22·85	32·46
P_2O_5	—	trace	1·86	0 67
SiO_2	----	1 20	7 12	—
SO_3	.	trace	trace	trace
FeS_2	- -	0·08	0 11	0·15
H_2O	—	—	2 97	1·43
Organic matter	--	trace	trace	2 95
Insoluble	—	3 77	1·64	7·29
	100 62	101 27	100 41	100·38
Total Fe	—	38 56	33·62	38·29

L. J. S.

CHAMOMILE FLOWERS. *Anthemis nobilis* An examination of the flowers of *Anthemis nobilis* (Linn) by Power and Browning (Chem Soc. Trans 1914, 105, 1833) has shown that these contain in addition to numerous other substances an *apigenin glucoside* $C_{21}H_{20}O_{10}·2H_2O$, faintly yellow microscopic crystals melting at 178°–180°. It dissolves in alkalis with a yellow colour and gives with aqueous ferric chloride a purplish-brown colouration. Dried at 125°–130°

it loses one molecule of water of crystallisation, but the second molecule cannot be eliminated without decomposing the substance. This is evident from the composition of the *hexa-acetyl* derivative $C_{21}H_{14}O_{10}(COCH_3)_6$, colourless microscopic crystals, m.p. 144°–146°, the molecule of water in question being eliminated in the process of acetylation.

By digestion with 5 p.c. aqueous sulphuric acid for three hours, this glucoside yields apigenin and dextrose according to the equation :

$$C_{21}H_{20}O_{10},H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$$

A. G. P.
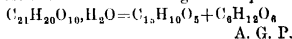
CHAMOMILE OIL *v.* OILS, ESSENTIAL.

CHAMOSITE, CHAMOISITE, *v.* THURINGITE.

CHAMOTTE. A mixture of fire clay and burnt pottery used for making fire bricks, crucibles, pipes, &c.

CHARCOAL *c* CARBON and FUEL.

CHARICIC ACID CHAVICIN *v. Pepper resin,* art. RESINS.

CHARTREUSE. A famous liqueur formerly prepared at the head-quarters of the Carthusian monks near Grenoble, but now, since the retreat of the monks from France in 1906, made at Tarragona in Spain

The recipe for the original liqueur or 'elixir vitæ' as it was called, was given by the Marquess d'Estrées to the Carthusian monks of Paris in 1602, but, owing to the difficulty of procuring the necessary alpine plants, they presented it to their brethren of the Grande Chartreuse in 1735.

The *elixir vitæ* was valued as a stimulant for the less robust members of the fraternity, weakened by age or by the privations and hardships entailed by the severity of their religious exercises, and was also dispensed to the feeble poor of the district.

After numerous disasters by fire, pillage, and confiscation of their property through religious and political persecutions, culminating in the loss of everything during the French Revolution, the monastery of La Grande Chartreuse was restored in 1816, although in a very impoverished condition.

Ingredients	Green	Yellow	White
China cinnamon	15 grams	15 grams	125 grams
Mace	15 ,,	15 ,,	30 ,,
Lemon balm, dried	500 ,,	250 ,,	250 ,,
Hyssop (flower tops)	250 ,,	125 ,,	135 ,,
Peppermint (dried)	250 ,,	—	—
Thyme	30 ,,	—	—
Balsime (*Bal major*)	125 ,,	—	—
Genepi	250 ,,	125 ,,	125 ,,
Arnica (flowers)	10 ,,	15 ,,	—
Balsam poplar (buds)	15 ,,	—	—
Angelica (seeds)	125 ,,	125 ,,	125 ,,
Angelica (roots)	62·5 ,,	30 ,,	30 ,,
Coriander	—	1500 ,,	—
Cloves	—	15 ,,	30 ,,
Aloes (Socotrine)	—	30 ,,	—
Cardamom (small)	—	50 ,,	30 ,,
Nutmegs	—	—	15 ,,
Calamus	—	—	300 ,,
Tonka beans	—	—	15 ,,
Alcohol at 85°	62·5 litres	42·5 litres	52·5 litres
White sugar	25·0 kilos.	25·0 kilos.	37·5 kilos.

The secret of the manufacture of the 'elixir' had, however, been carefully preserved, and this was made the basis of other varieties of liqueur, by the sale of which the monks hoped to improve their finances. The result was the production of green, yellow, and white 'chartreuse,' the virtues of which were advertised far and wide by the military officers who had been quartered in the monastery about the middle of last century. Extensive and modern plant was installed at Fourvoisie in 1863, and, in course of time, the sale of chartreuse increased the revenue of the monastery to a point it had never reached before.

After the passing of the French Religious Associations Act, in 1906, the monks of the Grande Chartreuse migrated across the border to Tarragona in Spain, carrying their secret formulæ with them.

More than 200 ingredients are said to be used in the manufacture of genuine chartreuse, and its spirit basis is rectified grape spirit distilled from sound wine. The usual alcoholic strength of the three varieties of chartreuse is : *green*, 55° of alcohol, or 96 p.c. of proof spirit ; *yellow*, 42·5° alcohol, or 74·5 p.c. proof spirit ; and *white*, 30° alcohol, or 52·5 p c of proof spirit.

There are innumerable imitations of chartreuse, mostly prepared from plain spirit flavoured with essential oils and coloured by means of the various ingredients described under CORDIALS AND LIQUEURS. The formulæ given in the table on p. 151 are amongst the best of those suggested for the preparation of imitation chartreuse.

Digest in the alcohol for 24 hours, distil until nearly all the spirit is over, and dilute to 100 litres. Colour green or yellow as described under CORDIALS and LIQUEURS, add the sugar, allow to rest till clear, and filter (*see* CORDIALS and LIQUEURS). J. C.

CHAULMOOGRA OIL GROUP.

This group is remarkable on account of the considerable optical activity which these oils exhibit, owing to the presence of the strongly active chaulmoogric and hydnocarpic acids (discovered by Power and his collaborators, Chem. Soc. Trans. 1910, 97, 1285). Hitherto, three oils belonging to this class have been described, viz. *Chaulmoogra oil*, obtained from the seeds of *Taraktogenos Kurzii* (King) ; *Hydnocarpus oil*, obtained from the seeds of *Hydnocarpus Wightiana* (Blume) ; and *Lukrabo oil*, the fat obtained from *Hydnocarpus anthelminticus* (Pierre). The saponification values of these oils lie between 204 and 213, and their iodine values between 90 and 86·4. The seeds of Taraktogenos contain a cyanogenetic glucoside. Chaulmoogra is chiefly used in the treatment of leprosy and various skin diseases in Indo-China, Siam, and to some extent also in Europe. A few years ago chaulmoogra oil was imported to the Continent as 'Cardamom oil' and used in margarine with disastrous results. Hydnocarpus oil, also known as *kavatel oil*, is occasionally sold as genuine chaulmoogra oil, but is inferior in its medicinal properties and contains a larger proportion of free fatty acids. The genuine oil from *T. Kurzii* is now official in the British Pharmacopœia, which describes it as a brownish-yellow soft fat, with a distinctive odour and acrid taste ; sp.gr. 0·940 at 45° ; m.p. 22°–30° ; iodine value,

96–104 ; acid value, 21–27 ; and saponification value, 198–213. It is partially soluble in cold and almost completely soluble in hot 90 p.c. alcohol. It is largely composed of the glycerides of acids of the chaulmoogric series, having the general formula $C_nH_{2-n_4}O_2$, and contains palmitin (Power, Amer. J. Pharm. 1915, 87, 493). Gynocardia oil, sometimes confused with chaulmoogra oil, is optically inactive. For an account of the origin of the confusion in the nomenclature of the acids derived from chaulmoogra oil and the oils which have been considered as identical with it, *see* Pyman, Reports of Progress of Applied Chemistry, 1916, 1, 292. J. L.

CHAULMOOGRIC ACID $C_{18}H_{32}O_2$.

An unsaturated acid found by Power and Gornall among the fatty acids contained in chaulmoogra oil from *Taraktogenos Kurzii* (King). Optically active $[\alpha]_D + 56°$; m.p. 68° ; b.p. 247°–248° (corr.)/20 mm. Easily soluble in chloroform and ether. Forms readily crystallisable salts with metallic bases, and esters with diphatic radicals (Chem. Soc. Trans. 1904, 838 and 851).

CHAY ROOT.

Chay root or Chay-aver (from *chaya* = which fixes colours, and *ver* = root) ; also called Indian madder, is the root of *Oldenlandia umbellata* (Linn.), Rubiaceæ. It bears the following Indian vernacular names : turbuli (*Bengali*) ; cheri-vello (*Telugu*) ; ché or chay, sayawer, imburel (*Tamil*). The plant is a small bush or herb found on sandy soils, chiefly near the sea-coast. It occurs in North Burma and Ceylon, but is most abundant in certain tracts of the Madras Presidency, from Orissa southward. It does not appear to be used in Bengal, but on the Malabar and Coromandel coasts, especially the latter, it is or was extensively cultivated, and employed in dyeing a colour analogous to Turkey-red. The chief market is Madras, where it was sold in small bundles at about 4d. a lb. The roots are usually about 10–12 ins. long and ¼ in. thick, somewhat straight and stiff, tough and wiry, and with few or no lateral fibres. When freshly gathered, they have an orange colour; but when dried and kept, they assume a yellowish-grey hue. Boiling water gives merely a pale-yellow extract, but if alkali is added, a blood-red decoction is soon obtained. The colouring principles seem to reside chiefly, if not entirely, in the bark of the root.

The older literature connected with chay root is extremely meagre, and is for the most part contained in the following publications : Philosophy of Permanent Colours, 2282, 1813, Bancroft ; Bulletin de la Société industrielle de Mulhouse, 5302, 1832, E. Schwartz and D. Koechlin ; L'Art de la Teinture des Laines, 475, 1849, Gonfreville. Quantities of the root were imported into Europe in 1774 and at later periods, and its dyeing properties were examined by the above-mentioned experts. It met with little practical application, however, as it was not found to possess any advantage over madder ; indeed, it was considered to have but one-half or even a fourth of the colouring power of madder ; further, it was found to contain certain undefined yellow substances of an acid character, which interfered somewhat with its dyeing power. Still, it was recognised as a good dyestuff, giving the usual madder colours, and equally fast to soap. It is evident that the

yellow substances referred to are not the same as those described in this article, as Schwartz states that they were present in larger quantity in ' nona ' (*Morinda citrifolia*) than in chay root, whereas the yellow substances described later exist in much larger quantity in chay root than in morinda root. Very probably they refer to Rochleder's ' rubichloric acid,' as this is contained in morinda root in larger amount than in chay root. Schützenberger, in his Traité des Matières colorantes, 2, 291, 1867, states that he found chay root to contain alizarin and chlorogenin (rubichloric acid) and that it was easy to exhaust the root by extraction with alcohol.

In many respects chay root resembles madder, as both contain ruberythric acid, alizarin, rubichloric acid, and cane sugar, but there are very marked differences in the nature of the other constituents of the two roots. Madder, as is well known, contains purpurin, purpurin- and purpuroxanthin-carboxylic acids, &c., and but traces of yellow crystalline substances, forming barium compounds soluble in water, which have not been fully investigated. In chay root the former substances are entirely absent, but, on the other hand, although the root contains considerable quantities of yellow crystalline substances, they are quite distinct from those contained in madder.

The phenolic constituents of this root have been studied by means of the sulphurous acid extraction method described in detail in connection with MADDER, and also by a subsequent exhaustion of the residual root with boiling lime-water in this manner, chlororubine, alizarin, and a mixture of non-tinctorial yellow substances were isolated. These latter are present in chay root (probably as glucoside) in comparatively large amount (1 p.c.), and have been shown to consist principally, if not entirely, of the following substances.

Alizarin a-methylether crystallises from dilute methyl alcohol in long orange-yellow needles, melting at 178°–179°. It has the constitution -
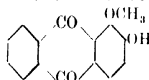
This compound may be synthesised by the action of an ethereal solution of diazomethane on a nitrobenzene solution of monoacetylalizarin (Oesch and Perkin, Chem. Soc. Proc. 1914, 30), subsequently removing the acetyl group. Owing to the fact that the so-called monoacetylalizarin is a mixture of the two monoacetylalizarins, both a- and β-alizarin methylethers are thus simultaneously produced. Addition of alcoholic potash to a solution of the product in alcohol causes the precipitation of the β-methylether as potassium salt, the a-methylether thus remaining in solution.

The methoxyl group present in this substance is much more readily hydrolysed than is usually the case, for prolonged digestion with boiling baryta water is sufficient for this purpose, a precipitate consisting of barium alizarate thus separating. This property, therefore, accounts for the difficulty in obtaining either this compound or alizarin dimethylether by means of methyl iodide, for in this process of methylation a prolonged digestion in the presence of free alkali is necessary. On the other hand, whereas

alizarin is only converted with considerable difficulty into alizarin dimethylether, by the action of methyl sulphate, alizarin a-methylether readily yields this substance when treated with this reagent in the usual manner.

Acetylalizarin a-methylether crystallises in yellow needles, melting at 212°.

Anthragallol dimethylether (A) forms yellow needles, and dissolves in alkaline solutions with a red colouration. It is distinguished from the isomeric compound described below, in that it yields an ammonium salt, crystallising in scarlet prisms, which is sparingly soluble in cold alcohol. Heated with sulphuric acid to 180°, or with hydrochloric acid, it is converted into anthragallol, and when methylated by means of methyl sulphate, is readily converted into anthragallol trimethylether. By the action of 10 p.c. potassium hydroxide in a sealed tube at 180° for 5 hours, it is partially converted into methoxyalizarin :
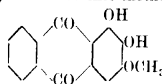
and a similar reaction occurs when sulphuric acid at 100° is employed. The constitution assigned to this anthragallol dimethylether (A), is therefore as follows :—
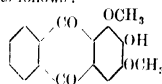
Anthragallol dimethylether (B) crystallises in yellow leaflets, melting at 230°–232°, and gives a red ammonium salt which is soluble in cold alcohol. Heated with 10 p.c. potassium hydroxide solution to 180° for 5 hours, it is partially converted into a compound having the reactions of methoxypurpuroxanthin
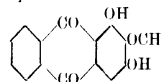
and most probably possesses the following constitution :—
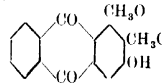
By methylation with methyl sulphate in the usual manner, this compound is readily converted into anthragallol trimethylether.

Acetylanthragallol dimethylether (B) consists of long yellow needles, melting at 176°–178°.

Hystazarine monomethylether obtained as long orange-yellow needles, melting at 232°, when heated with hydrochloric acid at 180°, is converted into hystazarine. Alkaline solutions dissolve it with a crimson colouration, and its ammonium and potassium salts, which crystallise in garnet-red needles, are insoluble in solid isobutylic alcohol. The constitution of hystazarine monomethylether is as follows :—
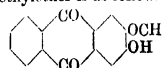
By means of methyl sulphate, it yields hystazarine dimethylether, which consists of yellow glistening needles, melting at 235°–236°.

Metahydroxyanthraquinone, pale - yellow needles, melting at 302°, is identical with the well-known artificial compound prepared from anthraquinone-β-monosulphonic acid by digestion with alkali.

Dyeing Properties.—Although chay root contains acid principles which tend to dissolve the mordants, its employment as a dyestuff presents no difficulty The only precautions necessary to be observed are to add 2 p.c. of chalk to the dye-bath, and to raise the temperature gradually to the boiling-point

Dyeing experiments on ordinary stripe-printed calico, containing alumina and iron mordants, have shown that the dyeing power of chay root is equivalent to the presence of a percentage of 0·33–0 35 alizarin. Compared with ground madder root of good quality, it seems to have about half its dyeing power when the comparison is made before soaping, but after soaping it appears to be quite equal to madder The reds, pinks, and chocolates have a distinctly bluer shade than those given by madder, and the lilacs are much fuller and brighter and very similar to those obtained from alizarin. This last feature alone ought to have secured a ready market for chay root among the European dyers, previous to the introduction of artificial alizarin, and it is somewhat strange that its marked suitability for lilacs should have escaped the observation of those who formerly made dyeing experiments with this root

On oil - prepared calico, mordanted with alumina, chay root gives an excellent blue shade of Turkey-red, withstanding the operation of clearing with soap and stannous chloride better even than a madder-dyed red, and quite equal to one obtained by means of artificial alizarin Good brown, red, orange, and purple colours are readily obtained on wool, and also on silk, suitably mordanted with chromium, aluminium, tin, and iron, according to the ordinary method usual with dyers. On wool, the colours not being submitted to any soaping operation, chay root appears to possess about half the dyeing power of madder.

Boiled with dilute sulphuric acid, chay root yields a 'garancine' of a very dark-green colour and possessing about three times the dyeing power of the original root.

Literature.—A. G. Perkin and J. J. Hummel, Chem. Soc. Trans. 1893, 63, 1160 ; *ibid.* 1895, 817 ; A. G. Perkin, *ibid.* 1907, 91, 2066 ; J. J. Hummel and A. G. Perkin, J. Soc. Chem. Ind. 1894, 13, 346   A. G. P.

CHEDDITE. An explosive consisting of a mixture of ammonium perchlorate, dinitrotoluene and castor oil (*v.* EXPLOSIVES).

CHEESE. A solid preparation of the chief constituents of milk, which, by the action of certain enzymes, are made digestible and palatable.

The action of enzymes is to a large extent influenced by the reaction or hydrogen ion concentration of the curd, which in turn is brought about by the extent to which the lactic organisms are controlled or encouraged in the process of manufacture.

Cheeses may be made from the milk of various animals, but they are usually prepared from cows' milk, which is either used in its natural condition, or may be first divided into cream and separated milk, from both of which products cheeses are also made.

In the case of cream and cottage cheeses, the lactic acid produced by the lactic ferments may be used for coagulating purposes ; but in the majority of cheeses, rennet is used to precipitate the casein. The caseinogen of the milk is converted into casein by the rennet ferment, and this, in the presence of the lime salts of the milk, is followed by the separation of insoluble calcium caseinate or curd, which carries with it nearly all the fat, some of the other constituents of the milk, and the enzymes of the rennet and milk. This curd differs from that produced by acids, which throw out caseinogen from the combinations with lime in which it occurs in milk.

The condition of the rennet curd, used for making different cheeses, is controlled by the acidity of the milk and by the temperature of renneting If milk is curdled with rennet without the previous development of acidity, a soft curd results ; this curd will not shrink so much as a curd produced from an acid milk. Too much acidity, on the other hand, results in a hard curd, which will shrink to a much greater extent, giving a hard ' acid ' curd.

Temperature also exerts an important influence in cheese making ; the action of the rennet is hastened up to about 100°F., and ceases at about 130°F The temperature employed, the degree of acidity, and the quantity of rennet used, will vary with different cheeses and also with the nature of the milk, the ash constituents probably exerting a considerable influence. The acidity is often controlled by the addition of ' starters,' *i e.* pure cultures of suitable lactic ferments or of mixed cultures in milk or whey, to the milk. The average temperature used is about 84°F., at which the coagulation takes some 40 to 60 minutes. In some cheeses, *e g* Leicester, Dutch cheeses, &c., annatto is added as colouring matter at least 10 minutes before the rennet. Salt is also added in the case of hard pressed cheese, when the curd has been ground prior to being put in the mould for pressing into shape ; in the case of soft cheese, about the time it is fit to take out of the mould.

With hard-pressed cheeses such as Cheddar, Cheshire, Derby, Leicester, Gloucester, Ementhaler, Gruyère, and Edam, the curd is cut up by means of curd knives, it is then stirred and heated to acquire the correct stage of dryness, consistency, and acidity, after which the whey is drawn off and the curd allowed to remain till a certain degree of acidity has developed. This is determined by means of a hot iron against which the curd is pressed, the length of the threads which are drawn out on pulling away the curd being taken as an index of the acidity produced ; the percentage of acidity at the various stages of manufacture may accurately be determined by means of the acidimeter. The curd is then ground in a mill, and afterwards pressed in a mould into a shape which varies with the different cheeses. After being pressed for 2 or 3 days, the cheese is ripened in a curing room, the humidity and temperature of which should be under control ;

a temperature of about 55° to 65°F. being most generally desirable.

To another group of cheeses, in which the process of manufacture varies considerably from the above, belong the moulded cheeses, in the making of which the pressing process is omitted, or in the case of Wensleydale greatly reduced ; the resulting cheese being softer and admitting of the growth of blue veins of mould (*Penicillium glaucum*) in the cracks left between the pieces of curd which extend throughout the cheese. To this group belong Stilton, Roquefort, Gorgonzola, Wensleydale, &c.

In the case of the small ' soft ' cheeses of the Camembert type, considerable variations are made in the process of manufacture, the resulting cheese being quickly ripened by moulds, or rather by the enzymes produced by moulds, which grow on the outside of the cheeses. *Penicillium candidum* and *Oidium Lactis* play an important part in the ripening of Camembert

Indole is present in Limburger and Camembert cheeses and in Handkase. Limburger cheese also contains phenol. Cheddar, Swiss, ' Gammalost,' Wick, and Roquefort cheeses do not contain indole or phenol Scatole is absent in all cases. The amount of indole in Limburger cheese increases during the ripening process until it reaches as much as 1 part in 52,800 parts of cheese (Nelson, J. Biol Chem. 1916, 24, 533) All cheeses contain *p*-hydroxyphenylethylamine, which is produced by the action of microorganisms on tyrosine ; the amine is a normal constituent of cheese, and is produced before actual decomposition of the latter takes place The organisms which produce the substance are probably identical with the *Baccaser-a-Freudenreich* (Ehrlich and Lange, Biochem. Zeitsch. 1914, 63, 156).

Tryptophane has also been found in ripe Stilton cheese.

The chemical analysis of cheese includes the determinations of the water, fat, total nitrogen, ash, and salt. The products of ripening are also sometimes determined, and the fat may be examined for adulteration with animal fats.

To determine the water, ash, and salt, 2 or 3 grams of well-sampled cheese, cut into small pieces, are weighed into a flat-bottomed dish and placed on the water-bath at 100°C., the dish being inclined so that the fat runs off the drying curd. Weighings are made every hour, and the water is found to have all been driven off in about 5 or 6 hours.

The melted fat is then poured off and the residue well macerated in hot amyl alcohol ; the residue may then be burnt and the ash weighed, the salt being afterwards dissolved out with water and the solution titrated with N/10 silver nitrate.

The water may be determined more rapidly by heating from 8 to 12 grams of the cheese with petroleum in a distilling flask connected with a condenser. In from 30 to 45 minutes the whole of the water will have been expelled and may be measured in a graduated tube (Analyst, 1913, 146).

According to Evans, Hastings, and Hart (J. Agric. Research, 1914, 2, 167), the organisms present in Cheddar cheese in such numbers as to indicate that they must have some function in the ripening process, are included in the four groups : *B. lactis acidi, B. casei, Streptococcus,* and *Micrococcus* ; each of these groups may be divided into a number of varieties according to their fermentative powers. The *B. casei* group is apparently responsible for the pungent taste which develops late in the ripening period. The action of two or more organisms growing together is not the sum of their individual actions when growing alone. When growing together, they may attack substances that neither can attack alone, or they may produce a larger quantity of acid than the sum of the quantities that either can produce alone.* The volatile acids formed in cheese result from the action of *Streptococci* and *Micrococci* on the citric acid, lactose, or protein present. One of the varieties of *Streptococcus b.* forms comparatively large quantities of alcohols and esters which contribute to the flavour of the cheese. The *B. casei* group of organisms form propionic acid, acetic acid, and lactic acid. Certain members of the *B. casei* group form *l*-lactic acid, and others form *d*-lactic acid ; a mixture of these organisms produces racemic lactic acid. The racemic lactic acid found in cheese during the curing process may also be produced to a small extent by enzymic acid, but it is more probably due to the combined action of *B lactis acidi* and the organisms of the *B. casei* group (J. Soc Chem Ind. 1915, 34, 97).

To obtain a typical Cheddar cheese from pasteurised milk, the pasteurising temperature should not exceed 88° (190°F.) when the milk is heated rapidly, or 77° (170°F.) when the time of heating is from 15 to 30 minutes. Heating to at least 77° (170°) is needed to reduce the number of organisms ; at 93° (200°F.) practically all the organisms are destroyed. Cheeses prepared from ' heated ' milk contained : water, 33·61–36·22 ; fat, 32·36–34·53 ; insoluble nitrogen (probably unaltered casein), 2·49–2·91 p.c. (Benson, J. Board Agric 1915, 21, 878).

Ether may be used to extract the fat, and the dried curd and fat afterwards weighed ; but a better method is to take a fresh portion of 3 or 4 grams of the cheese and grind with twice its weight of anhydrous copper sulphate in a small mortar, afterwards extracting with ether in a Soxhlet extractor.

Modifications of the Werner-Schmid or Gottheb-Rose methods also give good results.

The total nitrogen is determined by the Kjeldahl method in about 1 gram of cheese.

According to Richmond, the products of ripening may be determined in the following manner : 10 grams of the cheese are placed in a small mortar and ground up with 25 c.c. of boiling water ; the liquid is then decanted through a filter into a 250 c.c. flask, the process being repeated with nine further similar measures of boiling distilled water. The total filtrates are then cooled, made up to the 250 c.c. mark, and well mixed. The products of ripening are determined by the evaporation in a dish of an aliquot part (50 c.c.) ; this, after drying till constant at 100°C., is burnt, the weight of the dish and ash being subtracted from the weight of the dish and dry residue. The difference between 100 and the sum of the water, fat, ash, and products of ripening, may be taken as unaltered casein.

The primary products of ripening may be

determined in another 50 c.c. of the filtrate by the Ritthausen method as follows : 5 c.c. of copper sulphate solution are added and the solution neutralised with caustic soda solution ; the precipitate which forms is collected in a weighed Gooch crucible ; it is then washed well and dried in a water-oven, the fat is then extracted with ether, and the residue dried till constant. The crucible and its contents are then ignited and weighed, the difference giving the weight of the primary products of ripening, *i.e.* soluble proteins, &c.

To examine the fat, about 50 grams are dried till the fat runs out : the remaining fat is then extracted from the residue with ether, the ether evaporated and the fat examined, as in the case of butter fat. The soluble and insoluble acids and the Reichert-Wollny figure being generally determined, the addition of animal fats can be thus detected. The removal of fat from milk used in making cheese can be assumed if the fat is less than 45 p.c. of the dried cheese or less than six times the total nitrogen.

COMPOSITION OF CHEESE (BELL).

Description	100 parts contain					Proportion of fat in 100 parts of dry cheese	Proportion of fat in 100 parts of casein and fat	Salt per cent. in cheese	Percentage composition of fat	
	Water	Fat	Casein or nitrogenous matter	Free acid as lactic	Ash				Soluble acids	Insoluble acids
Stilton . .	23·57	39·13	32·55	1·24	3·51	51·19	52·50	0·67	4·42	88·96
American (red) .	28·63	38·24	29·64	—	4·49	53·57	52·12	0·72	4·26	89·66
American (pale) .	31·55	35·93	28·83	0·27	3·42	52·49	53·34	0·82	4·81	88·49
Roquefort . .	32·26	34·38	27·16	1·32	4·88	50·75	54·24	3·04	4·91	88·70
Gorgonzola . .	31·85	34·34	27·88	1·35	4·58	20·39	53·08	2·11	4·40	89·18
Cheddar (medium)	35·60	31·57	28·16	0·45	4·22	49·02	50·49	1·43	4·55	88·75
Gruyère . .	33·66	30·69	30·67	0·27	4·71	46·26	47·07	0·81	4·41	88·97
Cheshire . .	37·11	30·68	26·93	0·86	4·42	48·78	50·84	1·69	5·55	87·76
Single Gloster .	35·75	28·35	31·10	0·31	4·49	44·12	45·24	1·28	6·68	86·89
Dutch . .	41·30	22·78	28·25	0·57	7·10	38·80	42·41	4·45	5·84	87·58

The ripening process in cheese, whereby it usually acquires a more agreeable flavour, is essentially a fermentation of slow character, which is brought about by micro-organisms which are generally present in the milk or in the air of the dairy. They can only be controlled, to a limited extent, by the process of making, temperature, &c. It is not possible to destroy undesirable organisms by sterilisation, for heated milk will not make typical cheese as far as is at present known, though heating to 150°F. is now practised for soft cheeses. Cleanliness, from the moment the milk leaves the cow, is of the utmost importance.

The organisms which cause most trouble to the cheese maker are those which produce gas, which, when it develops in the curd, produces what is known as having or blown cheeses. These organisms, to which *Bacillus coli communis* belongs, often come from manure. Their absence can be demonstrated by what is known as a fermentation test, which consists in placing about 10 c.c. of the milk in a sterile test-tube and keeping it at blood heat for about 18 hours, after which time no signs of bubbles of gas should be seen in the tube.

Bitterness in cheese is sometimes caused by bacteria, as is the case when the milk is infected with *Micrococcus casei amari* or *Tyrothrix geniculatus*. An interesting example of a bitter cheese organism is that of *Torula amara*, which, after causing much trouble and loss in Canada, was eventually traced to the leaves of the sugar maple, from which source it infected the clean churns which were stood under the trees after being cleaned.

Discolouration of Stilton cheese may be

produced by two groups of bacteria acting upon caseinogen and certain amino acids.

Black spots in cheese may be caused by moulds or by particles of iron which get into the milk and are afterwards changed to sulphide by the sulphuretted hydrogen produced in ripening. Other organisms which produce colours (moulds, &c.), may get into the milk or may be derived from the air or utensils of the dairy at later stages of the manufacture.

The cheese maggot is the larva of the fly *Piophila casei*. There are four species of cheese mites : (1) *Carpoglyphus anonymus* (the Cheddar mite) ; (2) *Tyroglyphus siro* ; (3) *Tyroglyphus longior* ; (4) *Aleurobius farinæ* (2, 3, and 4 are Stilton and Cheddar mites) (N. B. Eales, 1917).

It must be remembered that micro-organisms and the enzymes they produce play a most important part in ripening ; for this process is also dependent on the proteolytic enzymes of the rennet and to the natural enzymes of the milk is not yet fully ascertained. As above mentioned, pure cultures of lactic acid organisms are sometimes added to milk to be used for hard-cheese making, and Camembert is often infected with the appropriate mould. Gorgonzola is also sometimes infected with mould to make the desired blue veins. As a general rule, however, the dairy and district where a particular kind of cheese is made contain the organisms which are necessary for the successful manufacture of the cheese in question.

The natural rind on Gorgonzola cheese amounts to from 2 to 4 p.c. of the weight, but in artificially coated cheese it may amount to from 16 to 27 p.c. of the whole weight. This

artificial coating consists of a mixture of barytes and tallow coloured on the outer side with oxide of iron. The importation of coated cheese into France is prohibited (Hinks, Analyst, 1911, 36, 61).

Oleomargarine and Lard Cheese. The success attending the sale of margarine as a substitute for butter has led manufacturers, especially in America, to introduce foreign fats of animal or vegetable origin in the production of cheese as a means of utilising skim-milk; the cream which has been abstracted being re placed by lard, oleomargarine, and by cotton-seed oil.

ANALYSES OF OLEOMARGARINE AND LARD CHEESES (BELL).

| | 100 parts of cheese contain | | | | Per cent. of salt | 100 parts of fat contain | | Melting-point of fat |
	Water	Fat	Casein and free acids	Ash		Insoluble fatty acids	Soluble fatty acids	
Oleomargarine	30·95	28·80	36·27	3·98	1·14	92·43	2·16	77°F.
Lard . .	31·30	24·66	38·87	5·17	1·55	92·88	1·55	92°F.

In flavour and character these samples closely resembled milk-fat cheese. Comparison of the results of the analysis of the two samples with those yielded by genuine cheeses in the former table conclusively proves the admixture with foreign fat. The low percentage of soluble acids indicates that more than one-half of the fat has not been derived from milk.   J. G.

CHEIRININE. See under CHEIROLINE.

CHEIROLINE $C_5H_9O_2NS_2$, colourless prisms, m.p. 47°–48°, optically inactive, occurs in wallflower seeds (*Cheiranthus Cheiri* [Linn.]), 1·6–1·7 p.c., and in *Erysimum* species. It has the constitution $CH_3 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NCS$ and has been synthesised (Schneider, Annalen, 1910, 375, 207). It is present as a sinigrin-like glucoside, which is hydrolysed by myrosin from white mustard seeds. Wallflower seeds contain an enzyme capable of liberating mustard oil from (myrosin-free) black mustard seeds (Schneider and Lohmann, Ber. 1912, 45, 2954). Cheiroline has no basic properties, and is said to be antipyretic (Wagner, Chem. Zeit. 1908, 32, 76). From wallflower leaves or seeds Reeb has obtained *cheirinine* $C_{14}H_{36}O_{17}N_3$, which resembles quinine in physiological action (Arch. expt. Path. Pharm. 1898, 41, 302; 1899, 43, 130) and a glucoside *cheiranthin*.   G. B.

CHELERYTHRINE $C_{21}H_{17}O_4N$ occurs in various Papaveraceous plants, *e.g. Chelidonium majus* (Linn.), *Glaucium flavum* (Crantz.), *Sanguinaria canadensis* (Linn.) (Probst, Annalen, 1839, 29, 120, 250), *Bocconia* spp. Forms colourless rhombohedra with $\frac{1}{2}H_2O$ or $1C_2H_5OH$, m.p. 203°, $[a]_D = 0°$. Salts intensely yellow and well crystallised. The free base is colourless. It contains a carbonyl group, and if this is altered the basic properties are lost. Perhaps it forms oxonium salts (Karrer, Ber. 1917, 50, 212). Contains two methoxy groups, and may be a methyl ether of sanguinarine (*q.v.*). Narcotic (König and Tietz, Arch. Pharm. 1893, 231, 145, 161; Murrill and Schlotterbeck, Ber. 1900, 33, 2802; Fischer, Arch. Pharm. 1901, 239, 409, 426, 438).

CHELIDONINE $C_{20}H_{19}O_5N,H_2O$ occurs with protopine, chelerythrine, sanguinarine, and a-, β-, and γ-homochelidonines in the root of the common celandine (*Chelidonium majus* [Linn.]), and with one or more of the same alkaloids in *Stylophorum diphyllum* (Nutt.) (Selle, Arch. Pharm. 1890, 228, 96), *Adlumia cirrhosa* (Rafin.) (*see* under *Adlumine*), and possibly in *Sanguinaria canadensis* (Linn.) (König and Tietz, Arch. Pharm. 1893, 231, 145, 161). It crystallises in monoclinic tablets, m.p. 135°–136°, $[a]_D + 115°$ 24′. Yields a benzoyl derivative, m.p. 217°, and when heated with zinc-dust furnishes ammonia and a substance with a phenanthrene-like odour (Schlotterbeck and Watkins, Pharm. Arch. 1903, 6, 141). Salts crystallise well (Wintgen, *ibid.* 1901, 239, 438). It is slightly toxic, resembling morphine in its action.

CHEMICAL AFFINITY. There has been much fruitless speculation about chemical affinity, about the nature of the force which impels two different substances to react with one another. During the last half-century, however, the efforts of physical chemists have been devoted rather to the practical investigation of the way in which chemical affinity manifests itself, and of the extent to which the operation of this force is modified by altering the external conditions. Quantitative methods have been devised for studying the influence of concentration, of temperature and pressure, and of foreign substances, on the course and products of a reaction. The object of this article is to give an outline of the methods employed and the results obtained in this study of the operation of chemical affinity. The three chief divisions into which the discussion of the subject naturally falls are (1) velocity of chemical reactions; (2) chemical equilibrium; (3) catalysis.

Velocity of chemical reactions. It is well known that different chemical reactions proceed to completion at very different rates. One change may be so rapid as to be practically instantaneous, whilst in another case the reacting substances may appear almost indifferent to each other. The rate of chemical change depends, however, to a marked extent on the temperature, so that the velocity of a reaction which takes place with extreme rapidity is moderated on lowering the temperature, and becomes amenable to experimental investigation. Suppose now that for such a reaction as that represented by the equation $A + B = C + D$, a range of temperature has been found over which the change proceeds at a measurable rate; the question next arises, How is the velocity of the change, at a given temperature, dependent on the quantities of the reacting substances A and B? In dealing with this

question, we shall assume that the reaction system is homogeneous, and that the change proceeds completely from left to right, *i.e.* until either A or B has disappeared.

The reaction system being homogeneous, it is permissible to regard matters from the molecular-kinetic point of view, and to conceive the interaction of the substances A and B as taking place only in so far as the molecules of A come in contact with the molecules of B. The velocity of the reaction, therefore—that is, the rate at which A and B disappear—will be proportional to the frequency of the collisions between a molecule of A and a molecule of B, even although only a certain proportion of the collisions is followed by chemical interaction. Now, on kinetic grounds, the frequency of the collisions between molecules of A and B is proportional to the product of their concentrations, hence the velocity of reaction between A and B is proportional to the product of their concentrations (or their 'active masses,' as it is sometimes put). This proposition is nothing else than the law of mass action, applied to the chemical change under consideration.

The foregoing proposition may be formulated in more definite shape. If a is the concentration of the substance A, and b is the concentration of the substance B at the beginning of the reaction, then the initial velocity of the change, V_0, is given by the equation $V_0 = k_1 \cdot ab$, where k_1 is a proportionality factor, the numerical value of which is independent of the concentrations of the reacting substances, and varies only with temperature and other external conditions. If, now, the reaction is allowed to proceed for an interval of time t, and if x represents the extent to which the concentrations of A and B have been diminished by the progress of the change, then the velocity at time t, V_t, is given by the equation $V_t = k_1 \cdot (a-x)(b-x)$. It is obvious that V_t must be less than V_0, and that the velocity of the reaction must diminish continuously from the start onwards : V_t, therefore, represents the velocity of the reaction only for an infinitely short space of time. This velocity is defined by the rate at which x is, at that moment, increasing with the time, and if, using the language of the differential calculus, we indicate by dx the extent to which x increases in the infinitely short space of time dt, we may write $V_t = \dfrac{dx}{dt} = k_1 \cdot (a-x)(b-x)$.

The applicability of the law of mass action, as expressed in the foregoing formula, is best appreciated by reference to a particular case, such as the inversion of sucrose. Although this change, which may be represented by the equation $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$, takes place with appreciable velocity only in the presence of a catalytic agent such as hydrochloric acid, yet the latter is found unaltered when the reaction is over, and the inversion of sucrose may be regarded as a particular case of the reaction $A+B=C+D$. The fact that the inversion is carried out in aqueous solution permits, however, a simplification of the formula $\dfrac{dx}{dt} = k_1 \cdot (a-x)(b-x)$; the water taking part in the reaction is a small fraction of the total water present, so that x may be neglected in comparison

with b, and we may write $\dfrac{dx}{dt} = k(a-x)$, where $k = k_1 \cdot b$. Integration of this equation leads to the formula $k = \dfrac{1}{t} \cdot \log_e \dfrac{a}{a-x}$, in which, as already indicated, a is the initial concentration of sucrose, and $a-x$ is its concentration after the inversion has proceeded for t units of time.

In order to test the validity of the formula $k = \dfrac{1}{t} \log_e \dfrac{a}{a-x}$ as applied to the inversion of sucrose, it is only necessary to ascertain the amount of sucrose still present in the reaction mixture at intervals during the progress of the inversion, and then to see whether the amount of sucrose varies with the time in the manner required by the formula. The simplest way of following the course of sugar inversion is to use the polarimeter. The reaction mixture, that is, sucrose solution containing a catalytic agent such as hydrochloric acid, is put in the polarimeter tube, which should be provided with a water-jacket in order to secure a constant temperature during the progress of the inversion. The angle of rotation is determined at the beginning of the change, at subsequent intervals, and finally when the change is complete. If we indicate by a_0, a, and a_∞, the initial angle of rotation, the angle at time t from the start, and the final angle respectively, then $a_0 - a_\infty$ is a measure of a, the total sucrose undergoing inversion, and $a - a_\infty$ is similarly a measure of $a-x$, the sucrose which has still to undergo inversion after time t. Hence $\dfrac{a}{a-x} = \dfrac{a_0 - a_\infty}{a-a_\infty}$ and the formula which should represent the course of the inversion becomes $k = \dfrac{1}{t} \cdot \log_e \dfrac{a_0 - a_\infty}{a-a_\infty}$. From the ascertained values of t, a_0, a, and a_∞, it is easy to discover whether the expression on the right-hand side of the equation is constant or not. The experimental data recorded in the following table show how far in a particular case the actual course of sucrose inversion corresponds with the velocity formula :—

Inversion of Sucrose at $25°$ by N/2 HCl.

t in minutes	Angle of rotation	$k = \dfrac{1}{t} \cdot \log_{10} \dfrac{a_0 - a_\infty}{a-a_\infty}$
0	$+25·16°$	—
56	$16·95°$	$0·00218$
116	$10·38°$	$0·00218$
176	$5·46°$	$0·00219$
236	$1·85°$	$0·00219$
371	$-3·28°$	$0·00221$
∞	$-8·38°$	—

The expression evaluated in the last column is $\dfrac{1}{t} \log_{10} \dfrac{a_0 - a_\infty}{a-a_\infty}$ instead of $\dfrac{1}{t} \cdot \log_e \dfrac{a_0 - a_\infty}{a-a_\infty}$, but, obviously, if the value of the former expression is constant, the value of the latter must be so also. The figures in the last column are satisfactorily constant, and the figure $0·00219$ may therefore be taken as the velocity coefficient for the inversion of sucrose under the specified conditions, viz. at $25°$ and in presence of N/2 HCl. The variation of the velocity coefficient with temperature and with the concentration of the acid will be discussed later.

Reactions, in which only one molecule of a single substance undergoes change, are termed *unimolecular* reactions, or reactions of *the first order*. The course of all such reactions, apart from possible disturbing factors, is represented by the formula $k = \frac{1}{t} \cdot \log_e \frac{a}{a-x}$. Examples of strictly unimolecular changes, to which the foregoing formula has been found applicable, are the transformation of acetochloramide into p-chloracetanilide, and Beckmann rearrangement, and the decomposition of nickel carbonyl. The inversion of sucrose is, strictly speaking, not a unimolecular but a bimolecular reaction, for both water molecules and sugar molecules are involved in the change. The reaction takes place, however, in aqueous solution, and, as already indicated, the consequence is that the course of the inversion conforms to that characteristic of a strictly unimolecular change In many other similar cases, a bimolecular reaction proceeds in accordance with the formula $k = \frac{1}{t} \log_e \frac{a}{x}$ Examples of this are the hydrolysis of methyl acetate and the decomposition of diazonium salts

It is desirable here to emphasise certain features which are characteristic of unimolecular reactions, features which can indeed be read out of the velocity formula, but are most clearly seen by the consideration of experimental data In the first place, for all unimolecular reactions the amount of change occurring in a given interval of time is a constant fraction of the unchanged substance still present This is a necessary consequence of the fundamental velocity equation, as is clear when it is written in the form $\frac{dx}{a-x} = k\,dt$, but the proposition is also in harmony with observation, as will be seen by a consideration of the following data bearing on the inversion of sucrose (Armstrong and Caldwell, Proc Roy Soc A 1905, 74, 199). A sucrose solution was inverted at 20° with hydrochloric acid, and the angle of rotation (a) was determined from time to time, with the results shown below :

Time	a
0	$+21\cdot55°$
15	$20\cdot40°$
120	$13\cdot75°$
135	$12\,95°$
225	$8\cdot62°$
240	$8\cdot02°$
∞	$-7\cdot18°$

The decrease in rotation during the first 15 minutes, viz. $1\cdot15°$, is a measure of the amount of change during that interval. The average rotation of the solution over this interval may be taken as $\frac{21\cdot55°+20\cdot40°}{2} = 20\cdot97°$, and a measure of the unchanged sucrose present is given by $20\cdot97+7\cdot18 = 28\cdot15$. The ratio of the amount of change occurring in the first 15 minutes to the amount of unchanged sucrose present is therefore $\frac{1\cdot15}{28\cdot15} = 0\cdot041$. If now the intervals from 120 to 135 minutes, and from 225 to 240 minutes are similarly considered, it will be found that the ratio of the amount of change occurring in the 15-minute interval to

the amount of unchanged sucrose present is $0\cdot039$ in each case, practically the same value as for the first 15 minutes of the inversion. The experimental data, therefore, bear out the statement that for a unimolecular reaction the amount of change occurring in a given interval of time is a constant fraction of the unchanged substance still present.

Another feature of unimolecular reactions is that the amount of substance changed in a given time is always the same *fraction* of the total amount of substance present at the beginning of the reaction, however this latter amount be varied. An illustration of this is furnished by the following data, referring to the inversion of sucrose in very dilute aqueous solution under the influence of invertase .—

Grams sucrose per 100 c c.	Grams sucrose inverted in 60 mins.
1 00	0·249
0 50	0·129
0·25	0·060

This experimental result is implied in the formula for a unimolecular reaction, for if $y = \frac{x}{a}$ is the fraction of the total sucrose which has been inverted up to time t, the formula may be written $k = \frac{1}{t} \log_e \frac{1}{1-y}$, and it is plain that the value of y depends merely on t, and is independent of a.

For bimolecular reactions, that is, reactions in which two molecules are concerned, the fundamental velocity equation is $\frac{dx}{dt} = k(a-x)(b-x)$, as indicated in the argument above. Integration of this equation leads to the formula $k = \frac{1}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}$. If, however, the two reacting substances have the same initial concentration, that is, if $a=b$, the integrated formula is $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$.

A typical case of a bimolecular reaction, or reaction of the second order, is the saponification of an ester by an alkali. Under suitable conditions of temperature and concentration, the velocity of saponification is measurable, and the progress of the reaction can be determined by extracting samples of the reaction mixture from time to time and titrating for free alkali. The figures in the following table, referring to the saponification of ethyl acetate by sodium hydroxide at 24·7°, will serve to show how far the experimental data are in harmony with the formula just recorded. The reaction mixture in this case was N/40 in relation both to ester and alkali, and the figures under $a-x$ in the table are the volumes of a standard acid solution required to neutralise 10 c.c. of the reaction mixture :—

t (min.)	$a-x$	$ka = \frac{1}{t} \cdot \frac{x}{a-x}$
0	8·04	—
4	5·30	0·129
6	4·58	0 126
8	3·91	0·132
10	3·51	0·129
12	3·12	0·131
15	2·74	0·129
20	2·22	0·131

The figures in the last column are satis-factorily constant, and confirm the application of the law of mass action to a bimolecular reaction.

Reactions of the third and higher orders are known and the formulæ applicable to these are obtained on the lines already indicated. Cases of such reactions, however, are comparatively rare, and it is not proposed to discuss them here. Investigation has shown that frequently a re-action which a general knowledge of the facts would lead us to regard as a reaction of a high order turns out to be one of a low order. This result is undoubtedly due to the apparently complex reaction being really a series of succes-sive changes of a simpler kind. Under these circumstances, the velocity of the complex re action is determined by those of the component reactions which are comparatively slow. If, for instance, one of the latter is incomparably slower than all the others, then the order of the complex reaction will be the order of this slow component reaction

Influence of Temperature.—It is well known that a chemical reaction is markedly accelerated by even a slight rise of temperature, but a definite measure of the influence of temperature on a given reaction can be obtained only by determining the velocity coefficient of the re-action at different temperatures. The value of the temperature coefficient of reaction velocity, deduced in this way, is remarkably independent of the nature of the particular reaction under investigation For homogeneous reactions of the most varied character, the factor by which the velocity coefficient at T^o must be multiplied in order to give the velocity coefficient at $T+10^o$, lies, as a rule, between 2 and 4. Speaking generally, one may say that the velocity of a chemical reaction is doubled or trebled for every rise of 10°. It is a striking fact that the temperature coefficient of various vital processes, such as vegetable respiration, is of the same order as that found for chemical reactions generally.

Chemical equilibrium. The reactions dis-cussed in the foregoing section have all been changes which proceed from left to right until at least one of the reacting substances has dis-appeared. There are many reactions, however, which do not belong to this type, inasmuch as they come to a stop while the reacting sub-stances are still present in the reaction mixture. Suppose, for instance, that the reaction between two substances A and B is of this description, and that C and D are the products of the re-action; then the change proceeds until a state of equilibrium is attained at which all four substances are present. It is further found that if the products C and D are brought together, they react to form the substances A and B, while the final state of equilibrium reached is the same as in the previous case Such a reaction is known as a *balanced* or *reversible* reaction, and in the corresponding equation a double arrow is substituted for the usual sign of equality; thus : $A+B \rightleftarrows C+D$.

The progress of a reversible reaction towards its equilibrium position may be regarded as the resultant of two opposed velocities, one the ve-locity (v_1) with which the substances on the left

side react to form those on the right side of the equation, and the other the velocity (v_2) with which the substances on the right side react to form those on the left side of the equation. If we take $A+B \rightleftarrows C+D$ to represent the reversible reaction in question, and suppose that at some particular moment the concentrations of the four substances in the reaction mixture are a, b, c, and d respectively, then at that moment $v_1 = k_1 ab$ and $v_2 = k_2 cd$. The observed velocity of the change is, of course, the difference between v_1 and v_2 If now the change has pro-ceeded at constant temperature until the equilibrium position is reached, and the con-centrations of the four substances are a_e, b_e, c_e, and d_e respectively, then $v_1 = k_1 a_e b_e$, and $v_2 = k_2 c_e d_e$. Since there is equilibrium, the forward reaction is exactly balanced by the back re-action, so that $v_1 = v_2$ and $k_1 a_e b_e = k_2 c_e d_e$, or $\dfrac{k_1}{k_2} = \dfrac{c_e \cdot d_e}{a_e \cdot b_e}$ If the ratio $\dfrac{k_1}{k_2}$ is replaced by the one

constant K, we have $K = \dfrac{c_e \cdot d_e}{a_e \cdot b_e}$. K is known as the *equilibrium constant*, and its numerical value defines the relationship which must exist between the equilibrium concentrations of the substances involved in a reversible reaction. The argument employed above might obviously be extended to reversible reactions other than $A+B \rightleftarrows C+D$: the result in all cases would be an equilibrium formula involving a constant ratio between the product of the equilibrium concentrations of the substances on the right side and the product of the equilibrium con-centrations of the substances on the left side, however the values of these concentrations might vary individually. It ought, perhaps, to be pointed out here that, in the equilibrium formula, the concentration of any substance, n molecules of which take part in the reaction, must be raised to the nth power.

In discussing the application of the law of mass action to reversible reactions with the help of the equilibrium formula, we shall deal first with cases in which the reaction system is homogeneous. As an example, the equilibrium between carbon dioxide, hydrogen, carbon monoxide, and water vapour may be considered ; the reaction in question is represented by the equation $CO_2 + H_2 \rightleftarrows CO + H_2O$, and is ob-viously of the type $A+B \rightleftarrows C+D$. In Hahn's in-vestigation of this equilibrium (Zeitsch. physikal. Chem. 1903, 44, 513), platinum was used as a catalytic agent, and on this ground the objection might be raised that the reaction as studied by that investigator is not really homogeneous. A true catalytic agent, however, as will be shown in greater detail at a later stage, does not affect the position of equilibrium in a reversible reaction, but merely lessens the time required for the attainment of equilibrium. The reaction which takes place between carbon dioxide and hydrogen, or between carbon monoxide and water vapour in contact with platinum, may therefore be regarded as a homo-geneous reaction. In Hahn's experiments, mixtures of the gases were passed through a heated quartz or porcelain tube containing spongy platinum. Provided that the rate of

passage was slow enough to allow the four gases to come into equilibrium with each other, analysis of the issuing gas gave the equilibrium concentrations, C_{CO_2}, C_{H_2}, C_{CO}, and C_{H_2O}. The relationship between these required by the law of mass action is $K = \dfrac{C_{CO} \cdot C_{H_2O}}{C_{CO_2} \cdot C_{H_2}}$, and the validity of the law in the case of this reaction is shown by the fact that the value of K obtained is, for a given temperature, the same when carbon dioxide and hydrogen, in varying proportions, are allowed to react, as when carbon monoxide and water vapour are taken as the initial substances. A few figures obtained by Hahn at 986° will serve to support this statement. Mixtures of carbon dioxide and hydrogen, in the proportions shown in the following table, were passed through the reaction vessel, and from analysis of the issuing gas the values of K were calculated by the above formula

Initial mixture		Equilibrium mixture			
CO₂	H₂	CO₂	CO = H₂O	H₂	K
10 1	89 9	0·70	9 46	80 38	1 59
30 1	69 9	7 18	23 00	46 82	1 58
49·1	51·9	21 36	27 88	22 88	1 59
60 9	39 1	34·20	26 61	12 58	1·64
70·3	29 7	47 66	22 79	6 76	1·61

Experiments were made, also at 986°, in which the initial mixture contained carbon monoxide and water vapour : the mean value of K, deduced from these experiments, was 1·55, slightly lower than the average of the figures recorded in the table The discrepancy, however, is not great, and the numerical data quoted suffice to show that the balance established between the four gases, whatever be their initial concentrations, is adequately defined by the mass action formula

A reversible reaction of great technical importance is the one which forms the basis of the sulphuric acid contact process

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$
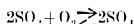
and consideration of this case from the standpoint of the mass action law throws light on many points connected with the process. The reaction may be regarded as a homogeneous one, for the catalysts used in the technical process do not affect the final balance between the gases, but only accelerate the attainment of equilibrium.

The application of the law of mass action, in this case, leads to the result $\dfrac{C^2_{SO_3}}{C^2_{SO_2} \cdot C_{O_2}} = $ const., in which C_{SO_3}, C_{SO_2}, and C_{O_2} are the equilibrium concentrations of the respective substances. It is convenient, however, to work with the reciprocal of the foregoing expression, and to regard the equilibrium constant as defined by $K = \dfrac{C^2_{SO_2} \cdot C_{O_2}}{C^2_{SO_3}}$. The accuracy of this formula may be tested with the help of the experimental data obtained by Bodenstein and Pohl (Zeitsch. Elektrochem. 1905, 11, 373). These investigators passed a mixture of sulphur dioxide and oxygen over spongy platinum, contained in heated quartz tubes, and determined the equi-

librium concentrations by analysing the issuing gas. The figures in the following table, obtained at 727°, show that the value of K, worked out from the equilibrium concentrations, is independent (1) of the relative proportions of sulphur dioxide and oxygen passed into the apparatus, (2) of the presence or absence of nitrogen :—

Initial gas ratio			
SO₂	O₂	N₂	K × 10²
0·21 :	1 :	0	3·49
0·62 :	1 :	0	3·59
1 20 :	1 :	0	3·48
1·68 :	1 :	0	3·51
3 97 :	1 :	0	3·67
1 23 :	1 ·	3·76	3·60
1 31 :	1 ·	3·76	3·54
1·55 :	1 :	3 76	3·52

The experiments showed also that the value of K obtained for a particular gas mixture was independent (1) of the direction in which the equilibrium position was approached, (2) of the rate at which the gaseous mixture was passed over the catalyst. The latter result is the guarantee that the equilibrium position was really attained.

Similar results were obtained at various other temperatures, and it was found that the value of K increased rapidly with rising temperature, as shown by the following figures :—

Temp. C.	K × 10³
528°	0 015
579°	0 077
627°	0 32
680°	1 12
727°	3 54
789°	12 6
832°	28 0
897°	81·6

This increase means that, as the temperature rises, the position of equilibrium is shifted in favour of the system $2SO_2 + O_2$; in other words, the dissociation of sulphur trioxide becomes greater. For each set of conditions, the extent of the dissociation is defined by the corresponding numerical value of K, deduced from a formula based on the foregoing table. It is possible, then, for a given temperature and given proportions of sulphur dioxide, oxygen and nitrogen in the initial gaseous mixture, to calculate what will be the relative quantities of trioxide and dioxide in the equilibrium mixture, that is, to calculate the 'yield' obtainable. The results of such calculations for various proportions of the gases and for various temperatures, are embodied in the following table. The numbers recorded in the last four columns are the percentages of sulphur dioxide convertible into sulphur trioxide under the specified conditions :—

Initial gaseous mixture			400°	500°	600°	700°
SO₂	O₂	N₂				
10·1 p.c.	5·05 p c	84·85 p c.	96·2	83·2	59·1	31·9
7·0	10 0	83·0	99·3	93 4	73·3	42·5
4·0	14·6	81·4	99·4	94 9	78·3	48·1
2·0	18 0	80·0	99·5	95·6	80·5	51·3

These figures bring out clearly one other point involved in the equilibrium formula, namely,

the influence of the partial pressure of the oxygen. If the equilibrium formula is written in the form

$$\frac{C_{SO_3}^2}{C_{SO_2}^2} = \frac{1}{K} \cdot Co_2 \text{ or } \frac{C_{SO_3}}{C_{SO_2}} = \frac{1}{\sqrt{K}} \cdot \sqrt{Co_2}$$

it is plain that the yield at a given temperature can be raised by increasing the partial pressure of the oxygen, and this conclusion is borne out by the foregoing table. The figures show also that the lower the temperature the better is the yield, but it must be remembered that from the technical point of view the time necessary for the attainment of equilibrium is also an important consideration. Fortunately, with platinum as catalyst, the union of sulphur dioxide and oxygen takes place with satisfactory rapidity, even at temperatures as low as 400°-500°, at which the dissociation of the trioxide is comparatively slight. With less active catalysts, however, such as ferric oxide, a higher temperature is required to secure a satisfactory velocity of reaction, and this involves a reduction of the obtainable yield.

Another reaction which is of exceptional interest from the standpoint of chemical equilibrium, and which has assumed great technical importance in recent years, is the synthesis of ammonia from nitrogen and hydrogen. Although, as Deville showed 50–60 years ago, even prolonged exposure of ammonia to electric sparks leaves a trace of the gas undecomposed, and a minute quantity of ammonia is formed, when a mixture of nitrogen and hydrogen is passed through a heated tube, it was not until the early years of the present century that the reversibility of the reaction was properly appreciated and an attempt made to apply the principles of chemical equilibrium. The physico-chemical investigation of the equilibrium $N_2 + 3H_2 \rightleftarrows 2NH_3$ has been carried out mainly by Haber and his collaborators (*see* Zeitsch. Elektrochem. 1914, 20, 597; 1915, 21, 89 128, 191, 206, 228, 241), but this research, conducted originally on purely scientific lines, has developed in a remarkably short space of time into a large scale process for the production of ammonia from its constituent elements.

Granted that there is a genuine equilibrium between nitrogen, hydrogen, and ammonia, Le Chatelier's principle indicates clearly that at any given temperature increase of pressure will shift the equilibrium position in favour of ammonia. The formulation of the equilibrium constant gives definite expression to this pressure effect, and for the present purpose the constant is best stated, not in terms of the equilibrium concentrations of nitrogen, hydrogen and ammonia, but in terms of their equilibrium partial pressures p_{N_2}, p_{H_2}, and p_{NH_3}.

On this basis $\dfrac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3}$ has a constant value at a given temperature, or alternatively,

$$K = \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} \cdot p_{H_2}^{\frac{3}{2}}}$$

Since at high temperatures the equilibrium concentration of ammonia is relatively small no great error is made, subject to that condition, by writing $p_{N_2} + p_{H_2} = P$, where P is the total pressure. If, further, the nitrogen and hydrogen have been taken in the exact proportions required by the chemical equation, $p_{H_2} = 3p_{N_2}$. When these relationships are coupled with the expression for the equilibrium constant it follows that $p_{NH_3} = 0.325K \times P^2$. Hence, for low concentrations of ammonia, the partial pressure of this gas in the equilibrium mixture is proportional to the square of the total pressure.

If x is taken to represent the volume percentage of ammonia in the equilibrium mixture,

$$x = \frac{p_{NH_3}}{P} \times 100 = 32.5K \times P \quad \text{This relationship,}$$

according to which the volume percentage of ammonia, for low concentrations, should be proportional to the total pressure, is confirmed, for example, by some of Haber's experiments at 800°, in which for P= 1 atmosphere, x was found to be 0.012, while for P=30 atmospheres x was 0.34.

The shift of the ammonia equilibrium with temperature is shown very clearly by the following table, in which the values of K, based on measurements carried out at a pressure of 30 atmospheres, are recorded for a number of temperatures :—

t° C.	561°	620°	700°	722°	801°	901°	952°
K > 10¹	21.3	12.6	6.80	5.82	3.56	2.13	1.68

From the graph based on the foregoing values it is possible to work out for various even temperatures and even pressures the maximum quantities of ammonia obtainable by the interaction of nitrogen and hydrogen under various conditions A selection of such figures, constituting a summary of the influence of pressure and temperature on the ammonia equilibrium, is embodied in the following table (valid for 1 vol nitrogen+3 vols. hydrogen) :—

EQUILIBRIUM PERCENTAGE OF AMMONIA.

Temp Cent.	at 1 atmo.	at 30 atmos	at 100 atmos	at 200 atmos
400°	0.44	10.7	25.1	36.3
500°	0.129	3.62	10.4	17.6
600°	0.049	1.43	4.47	8.25
700°	0.022	0.66	2.14	4.11
800°	0.012	0.35	1.15	2.24
900°	0.0069	0.21	0.68	1.34
1000°	0.0044	0.13	0.44	0.87

From the figures just quoted it is clear that the highest percentage conversion of nitrogen and hydrogen into ammonia is secured by working at a high pressure and a low temperature. In large-scale work, however, there is obviously a limit to the practicable pressure, and the pressure commonly employed in the technical process has been 150–200 atmospheres. A lower limit is likewise set to the temperature which can profitably be employed in practice by considerations of velocity. By themselves, nitrogen and hydrogen combine very slowly at temperatures below 1000°, and it is only in the presence of catalysts, such as osmium, uranium, and iron that the reaction is reasonably rapid at temperatures where the yield of ammonia is moderately satisfactory. A big yield and a

high velocity of reaction cannot be achieved simultaneously, and a balance has to be struck at the temperature which gives the best economic results. On the technical scale the temperature employed is generally 500°–600° C., and the mixed compressed gases are circulated over the heated catalyst in such a way that the ammonia formed is continuously removed by refrigeration or absorption. It should be pointed out that in the manufacturing operation the rate of passage of the gases over the catalyst may be too rapid to permit the reaching of equilibrium at each stage; it may be economically preferable to increase the rate of circulation and to be satisfied with a correspondingly smaller conversion at each contact with the catalyst (*see* Maxted, J. Soc. Chem. Ind. 1918, **37**, 232).

Many other dissociation equilibria, similar in type to the cases just discussed, have been successfully attacked from the standpoint of the law of mass action. One instance is the equilibrium $N_2O_4 \rightleftarrows 2NO_2$, a case in which a physical method, namely, the determination of the vapour density, must be employed to find the relative proportions of the reacting substances. Obviously, no direct chemical method of analysis is permissible in any case where the equilibrium shifts rapidly at the *ordinary* temperature, for such analysis involves the removal of one of the substances involved, and thus at once upsets the equilibrium.

Another technically important reaction, studied from the standpoint of the mass action law, is that which forms the basis of the Deacon process (*see* von Falckenstein, Zeitsch. physikal. Chem. 1907, **59**, 313; 1909, **65**, 371). When a mixture of hydrogen chloride and air is passed through a heated chamber containing bricks impregnated with cupric chloride, the hydrogen chloride and oxygen react, producing chlorine and water vapour, but the reaction comes to a stop before all the hydrogen chloride disappears; the reaction, in fact, is a reversible one, and may be represented thus :

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$
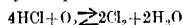
Experiments have shown that the equilibrium is defined by an equilibrium constant

$$K = \frac{C_{Cl_2}^2 \cdot C_{H_2O}^2}{C_{HCl}^4 \cdot C_{O_2}}$$

the value of which, at a given temperature, is the same, whether the initial gaseous mixture taken is hydrogen chloride and oxygen (air), or chlorine and water vapour. The value of K diminishes as the temperature rises, hence the extent to which hydrogen chloride can be converted into chlorine also diminishes with rising temperature. If x represents the fraction of hydrogen chloride convertible into chlorine, then the value of x can be calculated for any given temperature from the corresponding value of K and the partial pressure of the oxygen. For a dry mixture of 76·1 p.c. HCl and 23·9 p.c. O_2, the value of x is 0·865 at 352°, 0·79 at 430°, and 0·55 at 650°. If air is substituted for oxygen so that the ratio of hydrogen chloride and oxygen remains the same, the value of x is 0·71 at 430°. This is approximately the temperature employed

in the technical process, and the yield obtained is about 70 p.c. The use of lower temperatures, which would increase the yield, is precluded practically because of the much longer time required for the attainment of equilibrium.

The cases of equilibrium discussed so far have been those in which gases alone are involved. There are, however, many homogeneous reversible reactions in which liquid or dissolved substances take part. A classical example is the reaction between ethyl alcohol and acetic acid, represented thus :

$$CH_3 \cdot COOH + C_2H_5OH \rightleftarrows CH_3 \cdot COOC_2H_5 + H_2O$$
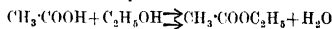
If 1 mol. of acid and 1 mol. of alcohol are heated in a sealed tube at 100° for a sufficient time, examination of the reaction mixture shows that it contains $\frac{1}{3}$ mol. each of acid and alcohol, and $\frac{2}{3}$ mol. each of ester and water. If then 1 mol. of ester and 1 mol. of water are mixed and treated in the same way, the equilibrium mixture finally obtained has the same composition as in the first case. The reaction therefore is truly reversible and the equilibrium constant is given by the equation $K = \frac{C_e \cdot C_w}{C_{ac} \cdot C_{al}}$, where C_e, C_w, C_{ac} and C_{al} are the equilibrium concentrations of the four substances. If v represents the volume of the equilibrium mixture in litres, then for the case where 1 mol. each of acid and alcohol are taken initially $C_e = C_w = \frac{2}{3}v$ and $C_{ac} = C_{al} = \frac{1}{3}v$, whence $K = 4$. It should be pointed out that the composition of the equilibrium mixture may safely be determined by titrating the free acetic acid, for the velocity of the reaction between ethyl alcohol and acetic acid is negligibly small at ordinary temperatures.

If the law of mass action is strictly applicable to the reaction under consideration, then the value of K obtained in experiments in which alcohol and acid are taken in other than molecular proportions should also be 4. Suppose, for instance, that m mols. of alcohol are allowed to act on 1 mol. of acid, and that after equilibrium has been reached, the fraction x of a mol. of ester has been produced; then $C_e = C_w = \frac{x}{v}$, $C_{ac} = \frac{1-x}{v}$, and $C_{al} = \frac{m-x}{v}$; so that $K = \frac{x^2}{(1-x)(m-x)}$. Instead of seeing whether the insertion of the known values of m and x in this formula gives the value 4 for K, the applicability of the mass action law may be tested by taking $K = 4$ and ascertaining whether the value of x calculated by the formula for a given value of m is in agreement with the value of x determined experimentally. This procedure has been adopted in the actual investigation of the case, with the following results :—

m	x found	x calc.
0·08	0·078	0·078
0 28	0·226	0·232
0·50	0·414	0·423
0·67	0·519	0·528
1·5	0·819	0·785
2·24	0·876	0·864
8·0	0·966	0·945

The excellent agreement of the figures in the second and third columns furnishes a convincing proof of the applicability of the law of mass action. The influence of 'mass' or concentration in affecting equilibrium is very clearly illustrated by the numbers quoted in the table, for it will be observed that when the amount of alcohol is great compared with the amount of acid, the latter is almost quantitatively converted into ester, in other words, the 'yield' of ester from acid is nearly theoretical

According to a widely accepted view, an electrolyte dissolved in water is dissociated into positively and negatively charged particles, called ions, and investigation of the conductivity of electrolytic solutions and of the abnormal effect of electrolytes on the freezing point and boiling-point of water supports the contention that the degree of this ionic dissociation increases with the dilution of the solution, and diminishes when the solution becomes more concentrated. The equilibrium, therefore, between the undissociated molecule of an electrolyte and the ions may be regarded as reversible and can be represented thus : $AB \rightleftarrows \overset{-}{A} + \overset{+}{B}$ If this view is correct, then, as Ostwald pointed out, the equilibrium should be governed by the law of mass action, and the relationship between the concentrations of AB, $\overset{-}{A}$, and $\overset{+}{B}$ at a given temperature must be defined by an equilibrium constant. Suppose, for instance, that acetic acid is the electrolyte in question, then the equilibrium is represented by

$$CH_3COOH \rightleftarrows \overset{-}{CH_3COO} + \overset{+}{H}$$
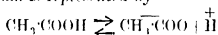
and the equilibrium formula will be $K = \dfrac{C_1 \cdot C_2}{C}$ where C, C_1, and C_2 are the concentrations of the undissociated molecules and of the two ions respectively. Since, however, the ions are produced in equivalent quantities, $C_1 = C_2$ and $K = \dfrac{C_1^2}{C}$. If we are dealing with a solution containing 1 gram-mol. of acetic acid in V litres of solution, and if we take α to indicate the fractional extent to which the molecules are dissociated, then in V litres there is $1 - \alpha$ gram-mol of undissociated acetic acid, and accordingly $C = \dfrac{1-\alpha}{V}$. Similarly, $C_1 = \dfrac{\alpha}{V}$, so that $K = \dfrac{\alpha^2}{(1-\alpha)V}$. For all binary electrolytes which, like acetic acid, dissociate into two ions, exactly the same formula would be obtained. The equation is the algebraic expression of what is known as Ostwald's Dilution Law, and K is usually termed a *dissociation constant* or an *ionisation constant* : it is also called an *affinity constant*

The determination of α is based on the relationship $\alpha = \dfrac{\Lambda}{\Lambda_\alpha}$, where Λ is the equivalent conductivity of the electrolyte at the dilution V, and Λ_α is the limiting maximum value of the equivalent conductivity. The application of the law of mass action to the equilibrium between acetic acid and its ions and to other similar cases is justified by the fact that the value of $\dfrac{\alpha^2}{(1-\alpha)V}$ is independent of the dilution at a given temperature. In support of this statement, the following figures for acetic acid may be quoted :—

V	$K \times 10^6$
16	1·79
32	1·82
64	1·79
128	1·79
256	1·80
512	1·80

An equally satisfactory constancy of the expression $\dfrac{\alpha^2}{(1-\alpha)V}$ has been observed in the case of all acids and bases which are dissociated to a comparatively small extent, and for these the validity of Ostwald's Dilution Law may be regarded as established For some reason, however, which has not yet been adequately explained, highly dissociated electrolytes, such as strong acids and bases and neutral salts, do not obey Ostwald's Dilution Law, although in the case of potassium chloride Weiland (J. Amer Chem Soc 1918, 40, 131) seems to have established the validity of the law for this compound at extreme dilutions.

Keeping in view this limitation to the validity of the formula $K = \dfrac{\alpha^2}{(1-\alpha)V}$, we may ask . What is the significance of the constant K ? The answer will be plain if two feebly dissociated acids, HA_1 and HA_2, are compared at the same dilution V. Since the acids are feebly dissociated, it is a very close approximation to the truth to put $1 - \alpha_1 = 1$ and $1 - \alpha_2 = 1$, so that $K_1 = \dfrac{\alpha_1^2}{V}$ and $K_2 = \dfrac{\alpha_2^2}{V}$. A comparison of the equations shows that the relative value of the dissociation constants is closely related to the degree of dissociation ; to put it generally, the dissociation constant is a measure of the ability of an acid to yield hydrogen ions, which, according to the modern view, are responsible for the characteristic properties of acids. The value of K for an acid is, therefore, a measure of its strength, of its power to manifest those properties which are associated with acids. One set of circumstances in which the relative strength of two acids is an important factor is realised when one gram equivalent of a base, such as sodium hydroxide, is added to a solution containing one gram equivalent of each of the two acids The base is insufficient to neutralise both acids, and the result is a competition between the two acids, each securing a fraction of the base. A theoretical discussion of this problem shows that if x is the fraction of the base appropriated by the first acid HA_1, and $1 - x$ accordingly the fraction appropriated by the other acid HA_2, then, provided the dilution is not too great, $\dfrac{x}{1-x} = \sqrt{\dfrac{K_1}{K_2}}$. If, therefore, the values of K_1 and K_2 have been determined in the way already described, it is possible to calculate the distribution of the available base between the two competing acids. That this can be done in good agreement with experiment is shown by the following figures :—

HA_1	HA_2	x calc.	x found
Dichloracetic acid	Lactic acid	0·95	0·91
Formic acid	Acetic acid	0·75	0·76
Acetic acid	Butyric acid	0·54	0·53

It is evident, then, that a knowledge of the dissociation constant of an acid enables us to calculate relatively the *affinity* or *avidity* of this acid for a base. There are other methods for ascertaining the relative affinity or avidity of an acid, methods available in the case of strong acids which do not obey the dilution law, and to which, therefore, no definite value of K can be assigned. Among these methods are the determination of the heat effects accompanying neutralisation (Thomsen), the measurement of the density changes (Ostwald), and the study of the influence of acids in accelerating the inversion of sucrose or the hydrolysis of methyl acetate. The *order* of magnitude of the values obtained by these and other methods for the relative affinity of acids is the same, as will be seen by an inspection of the following table :—

Acid	K × 100	Relative affinity deduced from	
		Sucrose inversion	Density changes
HCl	—	100	100
HNO₃	—	100	100
CCl₃COOH	30 (approx)	75	80
CHCl₂COOH	5 14	27	33
CH₂Cl COOH	0 155	4·8	7
HCOOH	0 021	1 5	3
CH₃COOH	0 0018	0·4	1

The manner in which a dissociation equilibrium is affected by excess of one of the products of dissociation has already been referred to in connection with the sulphuric acid contact process. It was there shown that as the equilibrium concentration of the oxygen is increased, so the extent to which the sulphur dioxide is converted into trioxide is increased also. In other words, the dissociation of sulphur trioxide into sulphur dioxide and oxygen is diminished in presence of excess of oxygen, one of the products of dissociation. An analogous statement may be made in connection with the electrolytic dissociation of an electrolyte, such as acetic acid. If to a solution of this acid a quantity of CH_3 COO ions is added, the dissociation of the acid is diminished to a large extent, *i.e.* the concentration of the hydrogen ions is very much reduced, and the acid character of the solution almost disappears. It is true that CH_3COO ions cannot be added by themselves, but a solution of the sodium salt of acetic acid serves the purpose, for such a salt, to judge from its conductivity, is highly dissociated into CH_3COO ions and sodium ions. That the effective acidity of an acetic acid solution almost disappears on the addition of a little sodium acetate solution is very clearly seen by comparing the effects of (1) the acetic acid solution, (2) the acetic acid solution + sodium acetate, on the inversion of sucrose. It has been found that the velocity of inversion in presence of

$$\frac{N}{4}CH_3 \cdot COOH + \frac{N}{4}CH_3 \cdot COONa$$
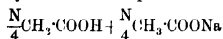
in about $\frac{1}{75}$ what it is in the presence of $\frac{N}{4}$ CH_3COOH alone. Not only is this influence of a neutral salt on the effective acidity of a weak acid to be expected on the basis of the mass action law, but it has also been found possible, with the help of the equilibrium formula, to calculate accurately the effect produced by adding any given quantity of the neutral salt.

The cases of equilibrium so far discussed have been those which occur in homogeneous systems, but there are numerous cases also of non-homogeneous or heterogeneous equilibrium. The bearing of the law of mass action on reversible reactions of this character will be most readily appreciated by considering one or two examples. The dissociation of calcium carbonate may be taken in the first place. If this substance is heated to 750° in a closed space, it breaks up to some extent into calcium oxide and carbon dioxide : if, on the other hand, carbon dioxide at atmospheric pressure is passed over calcium oxide, heated to the afore-mentioned temperature, the reverse action takes place and calcium carbonate is formed. That is to say, an equilibrium is established which may be represented thus : $CaCO_3 \rightleftarrows CaO + CO_2$. In applying the law of mass action to this case, we are confronted with the question : What is the concentration or 'active mass' of a solid taking part in a reaction ? An answer to this question may be reached by supposing that in the gaseous phase of the reaction system there is equilibrium between the calcium carbonate, the calcium oxide, and the carbon dioxide ; that is, each of the solid substances concerned in the reaction is supposed to have a definite, it infinitely small, sublimation pressure at a given temperature, and therefore to be represented in the gaseous phase. On this basis, the equilibrium at a given temperature would be governed by the formula $K_1 = \dfrac{C_2 C}{C_1}$, where C_1, C_2, and C are the equilibrium concentrations of calcium carbonate, calcium oxide, and carbon dioxide in the gaseous phase, respectively If partial pressures are employed instead of concentrations, the formula would be $K = \dfrac{\pi_2 \pi}{\pi_1}$. Now π_1 and π_2, being sublimation pressures, have fixed values at a given temperature, and are independent of the absolute amounts of calcium carbonate and calcium oxide present. Hence π = const., and since π_1 and π_2 are negligibly small, π, the partial pressure of the carbon dioxide, is practically equal to p, the total pressure exerted by the system ; so that we may write p = const. The application, therefore, of the law of mass action to the dissociation of calcium carbonate leads to the result that at each temperature the reaction system exerts a definite pressure—the dissociation pressure, as it is termed. This statement is valid only on the understanding that the substances involved in the reaction are kept in contact with each other ; if provision is made for keeping the pressure of the carbon dioxide permanently below or above the equilibrium value, then a reaction proceeds until the calcium carbonate (in the first case) or the calcium oxide (in the second case) has disappeared. By artificial alteration of the pressure at constant temperature, therefore, any reaction of the same type as $CaCO_3 \rightleftarrows CaO + CO_2$ may be made to proceed either from left to right, or *vice versâ*. The reaction $2BaO_2 \rightleftarrows 2BaO + O_2$ is also a case where two solids and a gas are in equilibrium

with each other, and it may be treated in the same way as the dissociation of calcium carbonate.

Perhaps the chief point that emerges from the foregoing is that the active mass of a solid taking part in a chemical reaction is constant. The correctness of this conclusion has been confirmed by the investigation of various heterogeneous reactions different in type from the dissociation of calcium carbonate. One of these may be considered here, viz. the equilibrium represented by $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$ (see Deville, Compt. rend. 1870, 70, 1105, 1201; 71, 30; Preuner, Zeitsch. physikal. Chem. 1904, 47, 385). On the assumption that the active masses of the iron and the iron oxide are constant, the application of the law of mass action obviously leads to the result $\dfrac{p_{H_2O}}{p_{H_2}} = \text{const.}$, p_{H_2O} and p_{H_2} being the partial pressures of the water vapour and the hydrogen when equilibrium has been established at a definite temperature. This relationship is verified by the experimental results, some of which are quoted in the following table. The experiments consisted in exposing iron in an electrically heated closed system to the action of water vapour kept up to a constant pressure (p_{H_2O}). From the total pressure reached at equilibrium— $p_{H_2O} + p_{H_2}$— the partial pressure of the hydrogen could easily be deduced. It was further found that, starting with excess of hydrogen and iron oxide, the equilibrium could be reached in the other direction. The results recorded in the table were obtained at a temperature of 900°; the pressures are given in millimetres of mercury :—

p_{H_2O}	p_{H_2}	$\dfrac{p_{H_2O}}{p_{H_2}}$
8·8	13·5	0·65
12·7	18·0	0·71
21·5	30·6	0·70
35·0	52·0	0·67
49·3	71·8	0·68

When the difficult nature of the experiments is taken into account, the numbers in the last column may be regarded as satisfactorily constant and as demonstrating the applicability of the mass action law to this case. Although in a closed system an equilibrium is reached in the way described, yet if provision is made for removing the hydrogen as fast as it is formed, and thereby keeping its partial pressure permanently below the equilibrium value, the reaction will proceed until the iron is all converted into oxide.

There are many reversible reactions involving a solid substance and a liquid, or a solid and a dissolved substance. Here also the active mass of the solid is constant at a given temperature, solubility and sublimation pressure being analogous quantities. The equilibrium formula undergoes, therefore, a similar simplification to that illustrated in the foregoing paragraphs.

Influence of Temperature.—In general, a reaction system which is in equilibrium at a given temperature is no longer in equilibrium when the temperature is altered. A measure of this influence of temperature on chemical equilibrium is found in the change of the equilibrium

constant, and an illustration of the extent to which K may change with temperature has already been given in connection with the oxidation of sulphur dioxide to trioxide. The exact relationship between temperature and equilibrium is defined by a formula associated with the name of van't Hoff, according to which

$$\frac{d(\log_e K)}{dT} = -\frac{q}{RT^2}.$$

The symbol K is the equilibrium constant, that is, the ratio between the product of the equilibrium concentrations of the substances on the right side of the equation and the product of the equilibrium concentrations of those on the left side; q is the heat evolved when the reaction goes completely from left to right, T is absolute temperature, and R is the gas constant. The theoretical basis of van't Hoff's formula need not be discussed here, but one or two points involved in it may be indicated. It is evident, in the first place, that when the heat effect of a reversible reaction is small, the variation in K is also small, i.e. the position of equilibrium is but slightly shifted on altering the temperature. An instance of this is furnished by the reversible reaction between ethyl alcohol and acetic acid. Again, if q is positive, $\dfrac{d(\log_e K)}{dT}$ is negative, so that K diminishes with rising temperature, corresponding to a shifting of the equilibrium in favour of the substances on the left side of the equation. If, on the other hand, q is negative, $\dfrac{d(\log_e K)}{dT}$ is positive, and a rise of temperature, therefore, involves a displacement of the equilibrium in favour of the substances on the right side of the equation. It will be observed that in both cases, whether q is positive or negative, a rise of temperature involves a shifting of the equilibrium in the direction which means absorption of heat.

As an illustration of the applicability of van't Hoff's formula in an individual case, the reaction $2SO_3 \rightleftarrows 2SO_2 + O_2$ may be taken. From the values of the equilibrium constant obtained for this reaction at different temperatures (see p. 161), the values of q over narrow intervals of temperature were calculated by the formula. It was found that q is a linear function of the temperature, and may, in fact, be represented by the equation $q = -47300 + 4T$. If this expression for q is inserted in the formula $\dfrac{d(\log_e K)}{dT} = -\dfrac{q}{RT_2}$, and the equation is integrated, the following formula is obtained :—

$$\log_{10} K = -\frac{10373}{T} - 2·222 \log_{10} T + 14·585$$

The relation between K and T expressed in this formula is almost exactly that observed in the experimental investigation : this appears from the following figures :—

$t°$ C.	log K found	log K calc.
528	- 4·809	−4·817
579	- 4·126	−4·099
627	−3·500	−3·502
680	−2·914	−2·893
727	−2·451	−2·453
789	−1·900	−1·922
832	−1·553	−1·573
897	−1·089	−1·083

Catalysis. No discussion of reaction velocity or chemical equilibrium would be complete without a reference to the phenomenon of catalysis. It very frequently happens that a chemical reaction, which of itself is extremely sluggish, proceeds with comparative rapidity in presence of some foreign substance—a *catalyst*, as it is called. Cases of such an acceleration of a chemical reaction have long been known, and in both laboratory and technical processes catalysts are in common use.

A rational quantitative study of catalysis is possible only on the basis of the law of mass action. In the velocity coefficient, as already explained, we have a definite measure of the rate of a chemical change under given conditions. For a given reaction, therefore, which is catalytically accelerated, the value of the velocity coefficient at a given temperature is a measure of the efficiency of the catalyst, and by comparing the values obtained for the velocity coefficient in different experiments, one can find out how the efficiency of a catalyst varies with the conditions under which it works, and how the efficiency of one catalyst compares with that of another working under the same conditions.

General Characteristics of Catalysis.—One very common and striking feature of catalysis is that the quantity of the catalyst is so small compared with the quantities of the main reacting substances. As a rule, too, the activity of the catalyst at the end of the reaction which it has accelerated is unimpaired. An illustration of these features of catalysis is furnished by the influence of colloidal platinum in promoting the union of hydrogen and oxygen at the ordinary temperature. In some experiments made by Bredig, 2·5 c.c. of colloidal platinum solution (containing 0·17 milligram of platinum) were shaken with electrolytic gas, with the following results :—

Time in minutes	Decrease in the volume of gas	Decrease per minute
10	17·8 c.c.	1·78
20	35 8 ,,	1 80
30	54 8 ,,	1·90
40	72·4 ,,	1·76
50	90·2 ,,	1 78

The average of the figures in the last column is a measure of the catalytic efficiency of the colloidal platinum in the early stages of its activity. The same colloidal platinum was then shaken intermittently during 14 days with the mixture of hydrogen and oxygen, about 10 litres of which disappeared in this time. Not only is the contrast between the minute quantity of the catalyst and the extent of the induced change sufficiently striking, but a determination of the actual rate of disappearance of the gas at the end of the 14 days showed that the rate of decrease, measured over successive 10-minute intervals, was 2·02, 1·87, 1·95, 1·97, and 2·01 c.c. per minute. From these figures it is obvious that the catalytic efficiency of the colloidal platinum is unimpaired. In connection with this case, however, the objection might be raised that hydrogen and oxygen do not combine at the ordinary temperature, and that the platinum ought to be regarded, not as accelerating a change which would take place in its absence, but as actually initiating the re-action. The answer is that at 500° hydrogen and oxygen combine with appreciable rapidity in the absence of a catalyst, but that, in view of the large temperature coefficient of reaction velocity, the rate of union naturally becomes insignificant even at 400°, whilst at ordinary temperatures the two gases appear not to react at all. There is, however, no reason to suppose that there is a definite temperature below which absolutely no combination takes place.

The mere fact that the amount of a catalyst may be almost infinitely small compared with the amounts of the substances changed under its influence, shows that the final state of the reactive system must be independent of the catalyst ; in particular, if the accelerated reaction is reversible, the state of equilibrium finally attained must be the same as when no catalyst is present. The catalyst, that is, influences only the rate at which the condition of equilibrium is reached, not the position of equilibrium itself. Experimental evidence in favour of this proposition is supplied by Turbaba's investigation of the relationship between aldehyde and paraldehyde. The conversion of paraldehyde into the equilibrium mixture, which at 50·5° contains 33·9 p.c. aldehyde, is accompanied by an expansion, and the course of the change may therefore be followed by means of a dilatometer. Various substances accelerate the change, but the difference between the initial and final volumes, as shown by the following figures, is independent of the nature and the amount of the catalyst :—

Catalyst	Per cent. of catalyst	Percentage increase of volume
Sulphur dioxide	0·08	8·20
,, ,,	0·07	8·34
,, ,,	0·002	8·19
Zinc sulphate	2·7	8·13
Hydrochloric acid	0·13	8·13
Oxalic acid	0·52	8·27
Phosphoric acid	0·54	8·10

If the position of equilibrium in a reversible reaction is independent of the catalyst, then K, the equilibrium constant, must be similarly independent. Further, since $K = \dfrac{k_1}{k_2}$, where k_1 and k_2 are the velocity coefficients of the forward and back reactions, it follows that the catalyst must accelerate the forward and the back reaction in the same proportion. This has been demonstrated in connection with the catalytic effect of acids on the action between an acid and an alcohol and the reverse change. It should further be pointed out that the amount of energy transformed during a chemical change, being dependent only on the initial and final states of the system, is independent of the catalyst. The latter may be compared to the oil which facilitates the sliding of a weight down an inclined plane, without affecting the total energy derivable from the fall of the weight.

Another point of great interest is the relationship between the value of the velocity coefficient for a given reaction at a given temperature and the concentration of the catalyst. In many cases the relationship is a linear one. The rate of inversion of sucrose by acids, for instance, is proportional to the concentration of

the hydrogen ions, provided that this concentration is low ; on the basis of this proportionality, in fact, it is possible to calculate the velocity of inversion by dilute acetic acid from the velocity observed with dilute hydrochloric acid. In other cases, however, the relationship between reaction velocity and concentration of catalyst is not a linear one. The decomposition of hydrogen peroxide under the influence of colloidal platinum is an illustration of this. The course of the decomposition can be followed by extracting a definite volume of the reaction mixture from time to time and titrating with potassium permanganate. The course of the change is in harmony with the formula for a unimolecular reaction, and for such concentration of platinum a definite value of k, the velocity coefficient, can be obtained. The following table contains the values of k corresponding to various concentrations of platinum : —

Platinum concentration	k
$21\ 0 \times 10^{-6}$	0·072
$10\ 5 \times 10^{-6}$	0 024
$5·2 \times 10^{-6}$	0 0084
$2·6 \times 10^{-6}$	0 0027

From these figures it appears that when the concentration of the catalyst is doubled, the velocity of decomposition is trebled

Catalysis and the law of mass action —The general characteristics of catalysts have been discussed in the foregoing paragraphs, but it must be admitted that the phenomena associated with catalysis are frequently more complex than has been suggested. It appears that the catalyst often works in such a way as to mask the operation of the law of mass action altogether Although a detailed discussion of these peculiarities of catalytically accelerated reactions is not possible here, a brief consideration of some typical cases will be found useful

An investigation has been made of the rate at which sulphur dioxide and oxygen unite in presence of platinum (*see* Bodenstein, Zeitsch. physikal Chem. 1907, 60, 1), and the results show that the velocity of union is independent of the oxygen concentration (except when it is extremely small), proportional to the concentration of sulphur dioxide, and inversely proportional to the square root of the trioxide concentration. This behaviour is obviously quite different from what would be expected under the law of mass action. The explanation adopted by Bodenstein is that the factor which really determines the velocity of reaction is the rate of passage of the sulphur dioxide through a layer of sulphur trioxide, absorbed at the surface of the platinum From this point of view, what is measured is a diffusion velocity, not a reaction velocity, for it is supposed that the sulphur dioxide and the oxygen, when they have reached the platinum, react with great rapidity Bodenstein has further shown that the rate of union of the two gases under the influence of other catalysts is governed by the same factors. Not only so, but it has been found that the rate of change in many other heterogeneous catalytic reactions is, in all probability, determined by the physical process of diffusion. This is the case with the union of hydrogen and oxygen in contact with heated porous porcelain (*see* Bone and Wheeler, Phil. Trans. 1906, 206, 1) ; in this

instance, the rate of union of the gases appears to be determined to a large extent by the rate of occlusion of hydrogen.

Additional support of the view that the velocity of a heterogeneous catalytic reaction may be determined mainly by a diffusion process, is furnished by the relatively low value of the temperature coefficient in these cases. As already indicated, the velocity of a homogeneous chemical reaction is doubled or trebled for every rise of $10°$, but the value of $\dfrac{k_{T+10}}{k_T}$ for a heterogeneous reaction is frequently not much greater than the value (about 1·3) we should expect if the rate of reaction were determined by a diffusion velocity alone

Among the most important catalytic reactions are those which take place under the influence of enzymes. These catalysts are able to promote changes in organic matter which, in their absence, can be effected only with great difficulty. There is a close analogy between enzymes and ordinary inorganic catalysts, but it is frequently found that, owing to the operation of various factors, the course of a reaction which takes place under the influence of an enzyme, deviates considerably from what we should expect on the basis of the law of mass action In the inversion of sucrose by invertase, for example, the velocity coefficient, calculated by the formula for a unimolecular reaction, increases with the time (Brown, Chem. Soc. Trans 1902, 373) This is shown by the following table, which refers to the inversion of a 9 48 p c sucrose solution at $30°$; the symbol x stands for the fraction of the total sucrose inverted by time t --

t min.	x	$\dfrac{1}{t} \log \dfrac{1}{1-x}$
30	0·265	0 00445
64	0 509	0 00483
120	0 794	0·00571
180	0·945	0 00698
240	0·983	0·00737

The departure from the law of mass action becomes still clearer when experiments are made in which a constant amount of invertase is allowed to act for a given time on varying amounts of sucrose in a constant volume of solution Such experiments show that the enzyme, instead of inverting a *constant fraction*, as required by the law of mass action, has inverted a *constant weight* of sucrose in the given time ; only when the quantity of sucrose is very small is the law of mass action obeyed. In the hydrolysis of starch by diastase, and of milk sugar by lactase, it is similarly found that the amount of change induced by the enzyme is, for the initial portion of the change, a linear function of the time (*see* Brown and Glendinning, Chem. Soc. Trans. 1902, 81, 388 ; E. F. Armstrong, Proc. Roy. Soc. 1904, 73, 500) ; the later portion of the change, when the amount of catalyst is larger relatively to the amount of carbohydrate, conforms to the law of mass action.

Another peculiarity about enzyme action, which is frequently observed, is that the activity of the enzyme does not remain constant throughout the whole course of the change which it induces. In the hydrolysis of amygdalin by emulsin, and of milk sugar by lactase, the

products of reaction seem to exert a specific influence in putting the enzyme out of action (*see* Tammann, Zeitsch. physikal. Chem. 1892, 13, 271 ; Armstrong, Proc. Roy. Soc. 1904, 73, 500). This is indicated by the regular falling off in the value of $\frac{1}{t} \log \frac{1}{1-x}$ as the reaction proceeds, that is, as the products of the reaction, accumulate.

Mechanism of catalysis.—Many theories have been advanced as to the way in which a catalyst exerts its influence. According to one very commonly accepted view, a catalyst is effective because it combines with the substrate, and this intermediate compound then breaks up into the final products of change, the catalyst being liberated. Obviously, if this account of catalytic change is to give an adequate interpretation of the phenomena, it must be supposed that the formation and decomposition of the intermediate compound together require a shorter time for their occurrence than the direct change itself. There is a good deal of evidence, largely of an indirect kind, in favour of the view that combination takes place between catalyst and substrate. The increased stability of invertase in presence of sucrose, the specificity of enzymes, and the occurrence of a linear portion in the time curve for the hydrolysis of sugars, are facts which contribute to this evidence. In the case of the catalytic influence of molybdic acid on the reaction between hydrogen peroxide and hydrogen iodide, it has been definitely shown that combination takes place between the molybdic acid and the hydrogen peroxide. Aluminium chloride also, well known as a catalytic agent, forms definite compounds with the substances the reactivity of which it promotes. But although we may frequently assume the very probable formation of intermediate compounds in enzyme action and catalysis generally, it is quite impossible, in many cases, to specify the nature of these compounds.

There are, moreover, many cases in which the efficiency of a catalyst depends almost certainly on something else than the formation of intermediate compounds. The investigation of non-homogeneous catalytic reactions, such as the combination of sulphur dioxide and oxygen under the influence of platinum, or the union of hydrogen and oxygen under the influence of porous porcelain, has led to the conviction that in these cases occlusion or adsorption of the reacting substances occurs at the surface of the catalyst, and that the higher concentration of the reagents thus secured is responsible for the greater velocity of reaction. It is possible to interpret enzyme action also on this basis, for the solution of an enzyme is, strictly speaking, a non-homogeneous system.

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CATALYSIS IN INDUSTRIAL CHEMISTRY.

Within the last two decades the applications of catalysis in industrial chemistry have undergone remarkable developments. Many catalytic processes are now in operation on the large scale for the production of both inorganic and organic substances, and the steadily increasing amount of research work done in this field of investigation will, without doubt, lead to the introduction of many other methods of manufacture based upon the influence of catalytic agents.

Methods of preparation of inorganic substances in which catalysts are employed are as yet comparatively few, but amongst them are included processes for the production of such indispensable materials as hydrogen, chlorine, sulphuric acid, ammonia, and nitric acid. In order to meet the growing demand for pure *hydrogen* various methods for the production of that element from water have been worked out, and several of these are based upon the fact that in presence of suitable catalysts steam and carbon monoxide interact at moderately high temperatures with the formation of hydrogen and carbon dioxide, which, of course, can be easily separated. Iron or other metals of the iron group serve as catalysts ; when the former is employed its activity is increased by the addition of small quantities of ' activators,' such as potassium hydroxide, or by using it in the form of an iron-copper couple. The reaction between steam and carbon monoxide may also be effected in presence of heated lime, preferably containing a small admixture of iron, or of a mixture of lime and charcoal.

Chlorine may be prepared catalytically by the well-known Deacon process, in which hydrochloric acid is oxidised by atmospheric oxygen in presence of cupric chloride at a temperature of about 400° ; and also by the method due to Hargreaves and Robinson, in which the reaction between sodium chloride, sulphur dioxide, and oxygen, which results in the formation of sodium sulphate and chlorine, is promoted by the presence of a catalyst such as cupric oxide.

In the contact process for the manufacture of *sulphuric acid* the primary reaction, viz. the formation of sulphuric anhydride by combination of sulphur dioxide with oxygen, is effected through the agency of platinum, although ferric oxide is also used as a catalyst. In the former case very complete preliminary purification of the gases is essential, since various impurities, and especially arsenic, even in minute quantities, quickly ' poison ' the catalyst and impair or destroy its activity.

The synthesis of *ammonia* is now carried out on a very large scale, since it has been discovered that when a highly compressed mixture of nitrogen and hydrogen is passed over a catalyst maintained at a temperature of 500°-600° the proportion of ammonia produced is sufficiently great to make the process remunerative. Even under the most favourable conditions most of the nitrogen and hydrogen remain uncombined, hence it is necessary to adopt a continuous process in which the residual gases are again passed over the catalyst after removal of the ammonia. Many different metals and other substances, e.g. metallic nitrides, have the power of catalysing this reaction, but it is understood that iron is employed in practice ; the metal is in a fine state of division and rendered active by the addition of a promoter.

When a mixture of nitrogen with oxygen or air is passed over a suitable catalyst at

temperatures of 500° and upwards nitric oxide is formed; excess of oxygen converts this compound into nitric peroxide, which, when dissolved in water, yields nitric acid and nitric oxide. The catalytic method of manufacturing *nitric acid* from ammonia is based upon these reactions. Originally platinum was used as the catalyst, but it has been found that iron activated with small quantities of bismuth or other substances is also very efficient. The mixed gases are passed over the heated catalyst with high velocity, hence a relatively small contact chamber suffices for the oxidation of comparatively large quantities of ammonia. So far as expenditure of power is concerned, this process is much more economical than the arc process, in which nitrogen and oxygen are caused to combine directly at a very high temperature.

Catalysts are also utilised in the manufacture of *graphite* from charcoal or coke in the electric furnace; in the preparation of *carbon tetrachloride*; in the *elimination of carbon disulphide from coal gas*; in the production of *sulphur* by limited combustion of sulphuretted hydrogen in the Claus kiln; in the preparation of *sulphuryl chloride*, of *hydrazine*, and of *aluminium nitride*; and in the electrolytic processes for the preparation of *hypochlorites*, *chlorates*, and *persulphates*, and for the regeneration of *chromic acid*. Moreover, it is claimed that they may be used with advantage in making *sodamide*, and in the manufacture of *alkali cyanides* by the action of nitrogen on heated mixtures of alkali carbonates and charcoal.

Largely as a result of the pioneer work of Sabatier and Senderens catalytic methods are likely to become of great importance in the domain of organic chemistry. Thus, for instance, hydrogen has been found available for many operations of reduction and of hydrogenation when used along with various catalysts. In the former class of reactions nickel is in general very effective, but as it is sensitive to 'poisons,' particularly the halogens, care must be taken that both the hydrogen and the substance to be attacked must be freed from such impurities. Palladium and platinum, especially when in the colloidal state, are very active catalysts of such reactions. The operations may be carried out either at the ordinary or at increased pressure, and either at such temperatures that the reacting substances are vaporised, or at the ordinary temperature with the substances in the liquid state or in solution. Among reducing actions of importance carried out at high temperatures may be mentioned the production of *methane* from carbon monoxide or dioxide, the preparation of *aromatic amines* from nitro compounds, and the reduction of aldehydes and ketones to alcohols. In the reduction of nitro compounds copper, either alone or with the addition of an activator, is an effective catalyst, but may be replaced by iron, nickel, silver, or gold. The hydrogen may be used by itself or mixed with steam, and in place of hydrogen mixtures of carbon monoxide and steam may be employed.

The preparation of *indigo white* may be quoted as an example of reduction at the ordinary temperature. Indigotin, suspended in a solution of sodium hydroxide, is rapidly reduced by hydrogen at 60°-80° in presence of active nickel; the catalyst is easily removed by filtration, and the solution of indigo white thus produced has the advantage of being free from any excess of the reducing agent. The process is applicable to the preparation of leuco derivatives of other vat dyes.

With nickel as catalyst the addition of hydrogen to unsaturated compounds, when in the state of vapour, is easily effected. Ethylene, for example, is readily converted into ethane at 200°, and the preparation of hexahydro derivatives of benzene and other aromatic compounds is carried out with little difficulty. In solution, and especially in presence of colloidal platinum or palladium, various alkaloids have been converted into hydro derivatives, which may prove of value medicinally, and a most useful application of the process of hydrogenation is the 'hardening of fats,' i.e. the conversion of oils or liquid fats into solid fats. This hardening process depends essentially upon the production of the solid glyceride tristearin by addition of hydrogen to the liquid glyceride triolein. Nickel is usually employed as the catalyst, but the oxide of nickel has also been recommended, and the use of a number of other metals (particularly those of the platinum group) and of their compounds has been patented.

A number of processes, in which reduction is effected by agents other than hydrogen, are also promoted by various catalysts. For example, in the reduction of azobenzene with sulphurous acid, the presence of a trace of hydriodic acid has a most beneficial effect, and the remarkable discovery has been made that the reduction of certain dyes with hydrosulphites or formaldehyde-sulphoxylates is greatly promoted by the addition of small quantities of certain other dyes. Moreover, in a number of electrolytic reduction processes, the presence of catalysts is advantageous; thus the electrolytic reduction of nitro-, nitroso-, or azo- compounds is facilitated by the addition of titanous salts, in very small quantity, to the liquid.

Many processes of oxidation are also induced or accelerated by catalysts. A well-known example of direct oxidation is the production of *formaldehyde* by passing a mixture of the vapour of methyl alcohol and air through a tube containing heated copper or platinum. *Acetaldehyde* is rapidly and smoothly converted into acetic acid by the action of a current of air if a little manganous acetate is dissolved in the aldehyde. *Anthraquinone* may be obtained by heating anthracene with oxygen, under pressure, if some cupric oxide or other catalyst is also present. In oxidations with sulphuric acid, as, for instance, the preparation of *phthalic acid* from naphthalene, the velocity of the reaction is in many cases greatly increased by the addition of small quantities of mercury or copper. If catalysts are present solutions of alkali chlorates readily act as oxidising agents in many cases where otherwise the reaction takes place slowly or not at all; thus a trace of vanadium pentoxide has a most advantageous effect in the preparation of aniline black by oxidising aniline with these reagents. Hydrogen peroxide is a most valuable oxidising agent for many hydroxy compounds if traces of ferrous salts are also present, and some processes in which oxidation is effected through the agency of nitrobenzene, e.g. the manufacture of magenta,

are promoted by the addition of ferrous salts which act catalytically as oxygen carriers. Moreover, electrolytic oxidation is frequently accelerated by catalysts; for example, in this method of preparing anthraquinone, a little ceric sulphate or chromic acid is added to the sulphuric acid in which the anthracene is suspended.

Catalysts are capable of promoting processes of dehydrogenation as well as of hydrogenation. For instance, an excellent method of obtaining *acetaldehyde* consists in passing the vapour of ethyl alcohol over copper heated to about 300°, and in a similar manner *ketones* may be prepared from secondary alcohols, *e.g.* camphor from borneol, with satisfactory results. *Hydrocarbons* also are dehydrogenated at comparatively low temperatures in presence of metals such as copper, nickel, or iron, and in this connection it should be noted that a number of patents have been taken out which cover the employment of these and other catalysts in the ' cracking ' of petroleum for the production of motor spirit, benzene, &c., from heavier oils.

Other reactions in which catalysts are effective include the hydration and the dehydration of organic compounds. An example of hydration is the preparation of *acetaldehyde* by inducing the combination of acetylene with water, which is carried out by passing a current of the gas into an aqueous solution of an acid in presence of a mercury salt which acts as the catalyst. The hydrolysis of esters, which may also be included in this category, finds practical illustration in the hydrolysis of fats into free fatty acids and glycerol by the action of water containing a small quantity of a catalyst, *e.g.* sulphophenylstearic acid. Dehydration is exemplified by the catalytic preparation of *ethylene* and other unsaturated hydrocarbons. Ethyl alcohol breaks down into ethylene and water when its vapour is passed over alumina heated to a temperature of 360°, and isoprene and other hydrocarbons of the same series can be obtained by a similar dehydration of dihydric alcohols. The catalytic influence of mineral acids in accelerating the formation of esters by the interaction of organic acids and alcohols is well known, and it has been found that acetaldehyde and ethyl alcohol readily react with formation of acetal in presence of calcium chloride and a trace of hydrochloric acid. Moreover, in many of the processes grouped under the heading ' condensation,' which find such extended application, there is no doubt that the condensing agent plays the part of a catalyst.

Much space would be required if an attempt were made to illustrate all the other kinds of reactions of organic compounds which are favourably influenced by catalysts, and it must suffice merely to indicate the employment of these agents in connection with the following operations: The preparation of aromatic hydrocarbons, *e.g.* of toluene by the action of methyl chloride on benzene in presence of aluminium chloride; the preparation of halogen derivatives of both aromatic and fatty compounds, when various catalysts known as halogen carriers are of the greatest service; the preparation of sulphonic acids derived from benzene and other hydrocarbons, from pyridine, &c.; the preparation of derivatives of amines or of amino- compounds, particularly of those in which aromatic radicals are introduced into the amino- group, *e.g.* the production of phenylanthranilic acid, which is easily effected by the addition of a small quantity of copper powder to a boiling solution of o-chlorobenzoic acid in aniline; the preparation of certain diazo- compounds, and the replacement of the diazo- group by the chlorine, bromine, or cyanogen radical; the preparation of aldehydes and ketones, *c.g* of benzaldehyde from benzylidene chloride or directly from benzene, and of acetone from acetic acid; the preparation of certain sulphur compounds, in which category the important methods of vulcanising rubber may be included. Moreover, in many cases, intramolecular rearrangements and polymerisations are accelerated by catalysts. The transformation of hydrazobenzene into benzidine under the influence of a strong acid, is a familiar example of the former class of change, whilst the latter is exemplified in the synthesis of various kinds of rubber by the polymerisation of butadiene and its homologues, which is promoted by the presence of sodium, acetic acid, and other catalysts, and in the conversion of acetaldehyde into para-acetaldehyde, ethyl acetate, or aldol.

Finally, it must be noted that a number of very important operations, for example, the manufacture of ethyl alcohol, are carried out through the agency of that group of catalysts produced by living organisms which are known as enzymes. In many respects the action of enzymes is similar to that of inorganic catalysts, and especially to that of colloidal platinum or palladium, but is specific in the sense that a definite enzyme is required to bring about a particular transformation.   G. G. H.

CHERRY. The fruit of *Prunus avium* (sweet cherry) or *P. cerasus* (Morella cherry). There are many varieties. König gives, as the composition of ordinary cherries:

Water	Protein	Free acid	Invert sugar	Sacch- arose	Other carbo- hydrates	Fibre	Ash
80·6	1·2	0·7	8·9	0·5	1·8	5·8	0·5

Included in the carbohydrates is 0·6–1·0 p.c. of pentosans '(Wittreann, 1901). A more detailed examination by Keim (Zeitsch, anal. Chem. 1891, 30, 401) showed that in the unripe fruit of *P. cerasus*, citric, malic, and succinic acids were present; that cane sugar was present, but diminished greatly as the fruit ripened. The ripe fruit contained no succinic acid, but malic and citric acid equal to 0·46 p.c. expressed as malic acid, were present, and the sugars were dextrose, levulose, and traces of inositol. Shaw (Expt. Station Record, 1899) found, as the mean of the analyses of 13 varieties of cherries:

Average weight	Whole fruit		Flesh		In the flesh			
	Flesh	Stone	Juice	Residue	Water	Protein	Sugar	Ash
5·29 grams .	93·9	6·1	86·4	13·6	81·3	0·9	11·2	0·5

Konig gives, as the mean of many analyses of cherry juice : Sp.gr. 1·0737 ; total solids, 19·4 ; sugar, 12·8 ; protein, 0·42 ; free acid, 0·75 ; tannin, 0·09 ; ash, 0·55, grammes per 100 c.c.

König gives, as the composition of the ash :

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	Mn_3O_4
Whole fruit .	54·8	4·4	5·8	5·4	1·5	15	6·5·4	5·0	1·6	8·0
Flesh only	50·1	—	7·0	5·2	—	12·9	—	—	—	—

The kernels of cherry stones contain .

Water	Protein	Fat	Nitrogen-free extract	Fibre	Ash
41·0	6·9	14·1	33·4	3·5	1·0

The kernels contain about 0·82 p.c. of amygdalin.

Dried cherries contain, according to analyses by Konig and Krauch (flesh only)

Water	Invert sugar	Other carbohydrates	Protein	Fat	Fibre	Ash
49·9	31·2	14·3	2·1	0·3	0·6	1·6

Willstatter and Zollinger (Annalen, 1916, 412, 164) find that the colouring matter of the skins of cherries is keracyanin, the chloride of which can be obtained in crystals containing either 4 mols. of water (red slender needles) or $3H_2O$ (stout brown prisms) The chloride has the composition $C_{27}H_{31}O_{15}Cl$, and is readily hydrolysed by boiling with hydrochloric acid, yielding cyanidin, dextrose, and rhamnose. Keracyanin is thus a diglucoside of cyanidin $C_{15}H_{10}O_6$, a frequent constituent of the colouring matter of flowers and fruits (v. ANTHOCYANINS. H I

CHERRY BARK TANNIN v. TANNINS.

CHERRY-LAUREL LEAVES. Laurocerasi folia (B.P.); leaves of Prunus Laurocerasus (Linn).

CHERRY LAUREL OIL v. OILS, ESSENTIAL.

CHERRY TREE GUM v. GUMS.

CHERT. (Feuerstein, Hornstein, Ger.) A silicious mineral allied to chalcedony and flint. Similar terms are applied to hornstone and to any impure flinty rock, including the jaspers It is worked extensively from carboniferous limestone quarries in Flintshire, especially at Halkin and Talacre in Denbighshire, Derbyshire, and at Reeth in Yorkshire. It is used in potteries for paving the mills in which flints are ground. The following is an analysis of a sample from Vizzin, Sicily, given by Ricciardi (Gazz. chim. ital. 11, 319):—

Interior

SiO_2	Al_2O_3	FeO	CaO	H_2O	Sp.gr. at 22°
96·31	0·30	0·25	0·47	2·81—100·14	2·572

White crust metamorphosed by heat

SiO_2	Al_2O_3	FeO	CaO	H_2O	Sp.gr at 22°
97·02	0·32	3·39	0·55	1·68=102·96	2·520

CHESSYLITE or **CHESSY COPPER.** (Kupferlasur, Ger.) A blue oxycarbonate of copper, $2CuCO_3·Cu(OH)_2$, found native at Chessy near Lyons (v. COPPER).

CHESTNUT. The sweet chestnut is the seed of Castanea vesca, the horse-chestnut that of Æsculus hippocastanum.

Average composition :

	Water	Protein	Fat	Carbohydrates	Fibre	Ash
Sweet chestnuts :						
Fresh kernels .	38·5	6·9	8·0	44·9		1·7
Dried kernels .	5·8	10·6	10·0	70·9		2·7
Spanish . .	10·0	0·3	7·5	68·1	2·4	2·7
Horse chestnuts	38·9	4·8	4·6	46·2	8·7	1·8
„ (air-dried)	14·8	6·8	5·1	68·3	2·7	2·2

Sweet chestnuts are largely used as human food ; the horse-chestnut has been tried as cattle food, with success (Gay, Ann. Agron. 1896, 22, 401 ; Auld, J. Soc. Chem. Ind. 1913, 32, 173).

The kernels of an aquatic plant, Trapa bispinosa, are extensively used as food under the name of water-chestnut, in the North West Provinces of India, being roasted and pounded to a flour. Hooper (Pharm. J. Trans. 1894, 53, 22) found this flour to contain :

Water	Protein	Fat	Sugar and gum	Starch	Cellulose	Ash
4·2	8·4	1·0	14·4	63·8	3·6	4·7

The ash of the flour contained a little manganese, which, however, was abundant in other parts of the plant.

The bark of the horse-chestnut, especially in early spring, contains æsculin $C_{15}H_{16}O_9$, the glucoside of æsculetin $C_9H_6O_4$. Another glucoside, argyræscin $C_{27}H_{42}O_{12}$, occurs in the seeds of the horse-chestnut (Rochleder, J. pr. Chem. 1862, 87, 1).

From the fat-free cotyledons two acids are obtained, viz æsculic acid, fine needles, m.p. 214° 215°, insoluble in water, forming yellow amorphous salts; and æsculinic acid, golden-yellow needles, m.p. 230°-231°, lævorotatory, soluble in water, forming yellow salts (Masson, Bull Sci Pharmacol 1918, 25, 65).

Sweet chestnuts contain small quantities of resins and tannin, and included in the carbohydrates are sugar, dextrin, starch, and other substances Very diverse amounts of these have been found by different observers. In the horse-chestnut, according to Laves (Zeitsch. angew Chem. 1902, 1013), there are about 50 p.c. starch, 14 p c. cane sugar, 13 p c glucose, and 0·2 p.c. tannin. H. I.

CHESTNUT EXTRACT. The wood of the Spanish chestnut, Castanea vesca, though it contains only 3-6 p.c of tannin, is the source of the much-valued chestnut extract The bark contains more tannin than the wood (17 p.c.), but is not much used The tree, which grows to from 60 to 80 feet in height, is abundant in Italy, the South of France, and Corsica, where it forms immense forests, and it is also very common in America.

Trimble (The Tannins), who very carefully examined the tannin, obtained analytical data and reactions which indicated that it was identical, or nearly so, with gallotannin, but it is probable that this wood also contains traces of a catechol tannin, for a certain quantity of a red-colouring matter is also present, which resembles in character a phlobophene. Some writers have suggested that chestnut tannin is a methyl ether of ordinary gallotannin, but there is apparently no definite evidence in support of this theory.

Chestnut is employed almost entirely in the form of extract, the strength of which varies, but usually contains from 26 to 32 p.c. of tannin. The extract is frequently decolourised, and sometimes mixed with quebracho extract and other materials. Chestnut tannin is the tannin which is most largely employed for the dyeing of silk. Castanea vesca appears to be frequently confused with the horse-chestnut, Æsculus hippocastanum. The tannin derived from this latter is, however, of little or no practical value (cf. Pollak, Collegium, 1913, 6, 291 ; J. Soc. Chem. Ind. 1913, 32, 706). A. G. P.

CHIAN TURPENTINE *v.* OLEO-RESINS.

CHICA RED AND CARAJURA. These are rare pigments prepared by the Indians of Central America from species of *Bignonia* which are very similar in appearance and may contain as a basis the same colouring matter. A red pigment of this character, evidently ' Chica red,' is referred to in The Travels and Researches of Baron Humbolt (Macgilivray, Edinburgh, 1836, p. 229) : ' Red paint is the ordinary decoration of these tribes. The most common kind is obtained from the seeds of the *Bixa-orellana* and is called annotto, achoute, or roucou. Another more expensive species is extracted from the leaves of the *Bignonia chica*.' According to Crookes (Dyeing and Calico Printing, 1874, 388) chica is obtained from the leaves of the *B chica* which the Indians boil with water, and add some particles of the bark known as ' aryane ' to the decanted liquid which causes the precipitation of the colouring matter.

An interesting *résumé* of what is known of this subject is given by Holmes (Pharm. J, 1901), who states that preparations very similar to carajura are employed by the South American Indians in Brazil, Bohvia, and Guiana These include chica from the leaves of *B. chica*, from ' ula ' leaves derived from an unknown species of *Bignonia* in Bohvia, and a pigment prepared from the heartwood of the *B tecoma* in Minas (Brazil) The latter, according to Lee (Chem Soc Trans. 1901, 284), is prepared by mixing the dust and shavings of this tree with slaked lime and heating the mass with water. From the *B tecoma* Lee isolated a considerable amount of a yellow crystalline compound, *tecomin* *c* BIGNONIA TECOMA.

Carajura or Crajura was apparently first examined by Virey (Journ. de Pharmacie et Chimie. (3) 5, 154). The sample experimented with, which came from Para, was soluble in alkalis and was precipitated therefrom by acid, and is stated to have been prepared by the Galibis by boiling with water the stem and leaves of an unknown species of *Bignonia* when the latter in the autumn had acquired a purple colour.

Crookes states (*loc. cit.*) that chica is soluble in 36 p.c. alcohol, in ether and in alkalis with a vinous red colour, and when heated in a sealed tube with alkali and glucose gives a bluish-red liquid which becomes brown on exposure to air and then yields on acidification an orange-red precipitate.

As the result of an examination of chica red or carajura said to be derived from the leaves of the *Bignonia chica*, Erdmann (Jahres. 1857, 487) assigned to the colouring matter which he isolated by extraction with alcohol the formula $C_8H_4O_3$. This substance was soluble in caustic alkali but not in alkali carbonate solutions, and when oxidised with chromic acid gave *anisic acid*, whereas with nitric acid picric acid was produced.

Perkin (Proc. Chem. Soc. 1914, 30, 212), who examined a sample of ' carajura ' obtained from Messrs. Wright, Layman, and Umney of London, and which is referred to in the paper of Holmes (*loc. cit.*), found this to contain a small quantity of the calcium lake of two colouring matters which had either been precipitated on, or inter-mingled with a substance of the nature of ground

bark or peat. After treatment with hot dilute hydrochloric acid, alcohol removes the colouring matters in the form of a resin, and from this, by means of boiling benzene, *carajurin* is isolated. This compound, to which the formula $C_{18}H_{16}O_5$ has been provisionally assigned, separates in ruby needles, melting at 204°–206°, is soluble in boiling dilute alkali with a red colour, and is nearly devoid of dyeing properties. With mineral acids it very readily yields oxonium salts, crystallising in bright, orange needles, of which the *sulphate*, probably $C_{18}H_{16}O_5 \cdot H_2SO_4 \cdot H_2O$ is the most stable, the *hydrobromide* and *hydrochloride* being decomposed at 100°. From the hydrochloride a *platinichloride* can be prepared. Cold acetic anhydride with a trace of pyridine, after two days, gives an almost colourless *acetyl* compound, crystallising in needles, whereas bromine gives an immediate precipitate with carajurin in acetic acid, which when boiled with this solvent, separates in orange needles. Hydriodic acid converts cara-jurin with loss of 2 molecules of methyl iodide and probably also of a molecule of water into a substance provisionally termed *carajuretin iodide*, bright scarlet needles, stable in the presence of cold water, and from this by means of cold pyridine, *carajuretin* $C_{16}H_{12}O_5$, scarlet needles, melting above 330°, and soluble in alkalis with a reddish-violet colour, is produced. By dry distillation carajurin evolves a trace of aromatic oil, resembling anisaldehyde in odour, and when fused with alkali, *p-hydroxybenzoic acid* and a colourless *substance*, melting at 185°–187°, as yet unidentified, are obtained. In many respects carajurin resembles the anhydro-hydroxybenzopyranol compounds described by Bülow and Wagner (Ber. 1901, 34, 1199).

That portion of the alcoholic extract insoluble in benzene yields to ether *carajurone*, isolated as a scarlet powder, which readily assumes a beetle-green lustre, and possesses strong dyeing properties Analysis indicates the presence of more oxygen in this compound than in carajurin. A small amount of a similar, but brighter lake from British Guiana, and obtained from the leaves of a ' bushrope,' gave a colouring matter dyeing alizarin-like shades. This preparation, considered to be ' chica red,' appeared to differ in some respects from the ' carajura ' above described.

Bignonia Tecoma. Tecomin. (*q.v.*)
A,G,P.

CHICAGO BLUE, -ORANGE, *v.* AZO-COLOURING MATTERS.

CHICK PEA. *Cicer arietinum*, L. A leguminous annual, growing to a height of about 2 feet, largely cultivated in India, where its seeds are used as food for cattle and horses, and, after the removal of the husks, for man.

In some cases the young leaves, fried in oil, are also eaten. Church (The Food Grains of India, 1886) gives, as the average composition of the seeds :

	Water	Protein	Fat	Sol. carbo-hydrates	Fibre	Ash
With husk	11·2	19·5	4·6	53·8	7·8	3·1
Husked	11·5	21·7	4·2	59·0	1·0	2·6

Analyses of various parts of the fresh plant were made by Passerini (Staz. Sper. Agrar. 21, 20 ; Chem. Soc. Abstr. 1893, ii. 226).

The fresh substance of the stems, leaves, and

entire pods contained 27·54 p.c., 24·39 p.c., and 19·85 p.c. of dry matter respectively.

The dry matter of the stems, leaves, and seeds contained:

	Protein	Fat	Cellulose	Other carbohydrates	Ash	Nitrogen
Stems	6·35	1·8	35·0	49·0	7·81	1·62
Leaves	14·21	4·1	13·9	58·9	8·83	2·27
Seeds	26·20	5·2	1·7	63·6	3·30	4·19

The ash contained:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl
Stems	48·4	0·5	23·6	4·4	2·1	0·03	5·3	5·8	6·2	3·7
Leaves	29·6	0·9	40·6	3·3	3·0	—	6·0	4·4	11·3	1·8
Seeds	24·6	1·3	4·5	20·0	2·4	—	39·6	3·4	0·7	2·9

Traces of boron, lithium, and copper were also present in the ash

A detailed analysis of the dry matter of the seeds was made by Zlataroff (Zeitsh. Nahr. Genussm. 1916, 31, 180), who found—fat, 6·30 p.c., starch 50·32 p c., fibre 3·62 p c., ash 2·87 p.c., total nitrogen 3·34 p.c., protein nitrogen 2·11 p.c., nuclein nitrogen 0·10 p.c., ammonia nitrogen 0·10 p.c., amide nitrogen 0·01 p c., amino-acid nitrogen 0·12 p c.; total phosphoric acid 0·998 p.c., inorganic phosphoric acid 0·118 p.c., organic soluble phosphoric acid 0·244 p.c, lecithin phosphoric acid 0·142 p.c., protein phosphoric acid 0·486 p.c. Oxalic acid (0·007 p.c.), citric acid, betaine, choline (0·02 p.c.), adenine, inositol and a phytosterol were also present.

H. I.

CHICLE. A gum imported into the United States for the manufacture of chewing gum. A sample from Yucatan contained: Acetone-soluble matter (resins) 40·0; gutta and carbohydrates 17·4; proteins 0·6; sand and foreign matter 2·3; water 35·0; ash 4·7 p.c.

For analytical methods of determining its value, see Dannerth, J. Ind. Eng. Chem. 1917, 9, 679; J. Soc. Chem. Ind. 1917, 971.

CHICORY or SUCCORY. *Cichorium Intybus* (Linn.). A perennial plant belonging to the *Compositæ*, growing to a height of about 3 feet, bearing blue flowers and having a long tap root. It is sometimes grown as cattle food, the foliage being thus used, but more generally it is cultivated for the sake of its root, which, when dried, roasted, and ground, is largely used for mixing with coffee. The blanched leaves are also used as a salad.

According to Letheby's analysis (quoted by Wynter Blyth, Foods, 359, 1909), fresh chicory roots contains:

Water	Gummy matter	Glucose	Bitter extractive	Fat	Cellulose, Inulin, and fibre	Ash
77·0	.7·5	1·1	4·0	0·6	9·0	0·8

Analyses by Mayer (Bied. Zentr. 1885, 828) gave:

Water	Albuminoids	Fat	Inulin	Fibre	Sugar	Bitter extract	Ash
72 to 77	1·1 to	0·2 to	12·0 to 17·3	1·4 to 1·8	5·6 to 6·0	0·5 to 0·15	1·4 to 1·9

Wolff (Chem. Zentr. 1899, ii. 211) also found that chicory root contains from 13 to 15 p.c. of inulin, and an optically inactive sugar, synanthrose. He states that drying the roots has little or no effect upon the sugars, but during roasting the reducing sugars are increased, a large portion of the inulin is changed, and caramel and dextrin are formed.

Even by storing a portion of the inulin is converted into inulide and some of the less readily fermented inulides undergo further degradation and are converted into the more readily fermented inulides. Wolff (Compt. rend. 1916, 164, 514) finds a substance which he calls *inulo-coagulase* in the root, which coagulates the inulin in the expressed juice. It is more abundant in the outer than in the central portions of the root and is destroyed by heating to about 60°. It does not coagulate starch, milk or pectin. In a later paper, Wolff and Geslin (Compt. rend. 1917, 165, 651; 1918, 166, 428) state that inulin breaks down, under the influence of an enzyme present in chicory root, to levulose with intermediate formation of inulides.

The bitter principle is believed to be a glucoside of levulose and a pyrocatechuic derivative, probably the aldehyde (Grafe, Biochem. Zeitsch. 1915, 68, 1). The determination of cupric reducing power affords a means of detecting the presence of chicory in coffee. The extractives of roasted coffee contain from 1·9 to 2·6 p.c. of reducing sugars, whilst the extractives of roasted chicory contain from 25·2 to 27·7 p.c. When the extractives of a coffee decoction yield more than 3 p.c. of their weight of reducing sugars the presence of chicory is indicated. The addition of cane sugar to the coffee does not affect the results and its presence may be detected by the polarimeter.

The presence of beetroot in ground chicory may be detected by washing the suspected sample with sodium hypochlorite solution until all soluble colouring matter has been removed, when the particles are to be examined under the microscope. If beetroot is present the particles will be seen to contain numerous black cells filled with crystals of calcium oxalate. The cells are oval or elongated and are more numerous near the ligneous vessels of the woody portion of the root (Collin. Ann. Falsif. 1916, 9, 271).

Petermann (Bied. Zentr. 1883, 843) found pure roasted chicory to contain:

Soluble in water, 74·2 p.c.

Water	Glucose	Dextrin and inulin	Protein	Colouring matter	Ash
16·3	26·1	9·6	3·2	16·4	2·6

Insoluble in water, 25·8 p.c.

Protein	Fat	Cellulose	Ash
3·2	5·7	12·3	4·6

The ash of chicory root and leaves, according to Wolff, contains:

	K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Root	40·4	7·7	6·3	8·7	3·0	14·2	9·0	6·0	3·7
Leaves	60·0	0·7	3·2	14·3	—	9·0	9·0	1·0	1·7

Wynter Blyth (Foods, 359, 1909) gives as the main differences between the ashes of coffee and chicory, the following :—

	Coffee ash	Chicory ash	
Silica and sand	—	10·7–35·9	p.c.
Carbon dioxide	14·9	1·8–3·2	,,
Ferric oxide	0·44–0·98	3·1–5·3	,,
Chlorine	0·26–1·1	3·3–4·9	,,
Phosphorus pentoxide	10·0–11·0	5·0–6·0	,,

The soluble ash of chicory may be taken as about 1·74 p.c., that of coffee as about 3·0 p.c.

Chicory has about three times the tinctorial power of ordinary coffee, and this has been proposed as the basis for a rough estimation of the amount of chicory present in a mixture of coffee and chicory (Leebody, Chem. News, 30, 243).

The sp.gr. at 15·5° of a solution, made by boiling a quantity of the substance with ten times its weight of water, affords a ready method of approximately determining the amount of adulteration. The following table gives the specific gravities of infusions made in this way from the various substances :—

Spent tan	.	.	.	.	1·00214
Acorns	.	.	.	.	1·00730
Peas	.	.	.	.	1·00730
Mocha coffee	.	.	.	1·00800
Ceylon coffee	.	.	.	1·00870
Java coffee	.	.	.	1·00870
Costa Rica coffee	.	.	.	1·00900
Native Ceylon coffee	.	.	1·00900
Brown malt	.	.	.	1·01090
Black malt	.	.	.	1·02120
Dandelion root	.	.	.	1·02190
Red beet	.	.	.	1·02210
Yorkshire chicory	.	.	.	1·01910
Foreign chicory	.	.	.	1·02260
Guernsey chicory	.	.	.	1·02326
Maize	.	.	.	.	1·02530
Bread raspings	.	.	.	1·02630

(quoted by Wynter Blyth, Foods, 360).

Hehner and Skertchly propose a determination of furfural (a measure of pentosans) as a means of examining suspected coffee. Coffee gives about 5–5·5 p.c., chicory about 2·5 p.c. of pentosans (Analyst, 24, 178). H. I.

CHILE SALTPETRE. *Sodium nitrate* (*v.* SODIUM).

CHINA BLUE. Syn. *Water Blue, Cotton Blue, Opal Blue* v. TRIPHENYLMETHANE COLOURING MATTERS.

CHINA CLAY or KAOLIN v. CLAY.

CHINA GRASS. *Rhea Ramie fibre.* This substance is the fibre of two (or perhaps more) species or varieties of the genus *Boehmeria*, nat. ord. *Urticaceæ*, shrubs allied to the nettle (*Urtica*), but possessing no stings, namely, *Boehmeria nivea* (Hook and Arn.) with a white hairy under surface to the leaf, and *B. utilis* [*B. tenacissima* (Gaud.)] with a green (Blume) under surface (more or less hairy only on the nerns) to the leaf. It is the Tchou-ma of China and the Rheea of Assam. The plants grow to a height of from three to five feet, throwing up numerous straight shoots as thick as the little finger, and covered with short soft hairs. Its leaves grow upon long foot-stalks and are broadly heart-shaped, about six inches long by four broad. It is a native of China and Sumatra, where, as in India, it has long been cultivated.

Its manufacture into mats used for making sails, foot-mats, &c., is carried on in Southern China, where three crops of Tchou-ma are taken each year, of which the second is the best. For this purpose the grass is sorted into bundles, which are soaked in water for two or three days and then dried in the sun. If a red colour is desired, the grass is steeped in a decoction of sapan wood ; if yellow, in a decoction of the seeds and flowers of the common Chinese plant *mi-fa*, or in one of *Sophora japonica*, to which a little alum is added as a mordant. Other vegetable dyes are also employed ; but of late years aniline colours have in a measure taken their place.

By processes of manufacture an exceedingly fine fibre is produced on separating the filaments of the stalk—a fibre distinguished by its strength, which is nearly three times that of Russian hemp ; by its length, which is greater than that of any bast product ; and by its lustrous, silky appearance. Great efforts have been made, with more or less success, to render the use of the fibre in European textile manufactures commercially profitable. It will be seen from the following remarks that there are difficulties in the way. In the first place, the method of separating the bast by hand was tedious, and could only be performed whilst the stems were quite fresh, thus limiting its production to the immediate neighbourhood of the plant's growth. In China the bark is stripped from the stems and the fibre scraped off with a knife, a process which removes the whole so-called grass if performed while the stem is still quite fresh, but leaves a large portion if it has become at all dry. Even under the best conditions a very skilful operator can collect only two pounds of grass per day, the average quantity obtained being only half a pound to one pound. It is further found that, owing to the large amount of pectinic substances contained in these *Urticaceæ*, the long steeping or rotting processes used with flax and hemp cannot be practised on account of the ensuing excessive fermentation, which injures the fibre. Experiments made in India with unskilled workers gave about four ounces per day each as the result of their labour. Attention has consequently been given to mechanical processes for separating the fibres from the bark in the green and in the dry state. With this in view, the India Office some years ago submitted samples of the dried article to Dr. Forbes Watson, who reported that he did not find it at all difficult to obtain the fibre from stems which were quite dry. The difficulty in the case of India is that the best crops are obtained during the rainy season, when it is all but impossible to dry the stems except by expensive artificial means ; while, as above pointed out, the liability of the plant to ferment resulted in the spoiling of the crops when its treatment was delayed. The Government of India has followed up its inquiries and encouraged inventors to competition in producing a machine capable of dealing with the green crop. It may be said that this encouragement has resulted in an approximation to success ; thus, in one instance of a machine consisting of a cylinder with beaters revolving at a high speed against the stems upon which meanwhile a jet of water is poured, Dr. Watson estimated the cost of producing the fibre to average 4l. to 5l. per ton. The yield from the machine was from 1 to 2 tons of green stalks per day, estimated to produce about 100 lbs. of cleaned fibre.

In the treatment of green stalks by hand the Favier's process consists in subjecting the plants to the action of steam for 15 to 30 minutes, after which the bark is easily stripped. Those stems also which have been standing

some time after being cut can also be treated without leaving any appreciable amount of fibre on the stalks.

The operation of scutching the dried stems presents no difficulty when steam power is applicable and when the quantity of material to be treated is sufficiently large. The next process, however, of 'ungumming' has given a little trouble. Since China grass contains from 22 to 28 or, in some cases, up to 35 p.c. of gum, it is necessary to remove this constituent of the fibre before it can be spun into yarn. For this purpose many partly mechanical and partly chemical processes have been devised. It may sufficiently describe the lines which these various systems take to say that they resemble generally the processes adopted in the scouring and bleaching of cotton goods—that is to say, by subjecting the material to pressure under the application of steam, and to alternate treatment of alkaline and acid agents.

American inventors have devised means by which the fibre can be spun in ordinary cotton machinery. Rossi, of Naples, has patented a method by which China grass can be retted without chemical agents. When chemically degummed ramie is manufactured in combination with cotton and dyed and printed, the goods possess a silky lustre which enhances the colours on both fibres.

China grass has little or no attraction for dyes, and consequently the methods adopted in the dyeing of cotton or of jute are applicable to it. It is found that mineral colours, such as chrome yellow and orange, destroy the peculiar lustre of China grass; the yellow dye obtained with cadmium sulphide, however, is not open to this objection. Alizarin mordanted with Turkey-red oil destroys the lustre, whilst aniline colours fixed with the same mordant do not. Rosaniline derivatives and azo- colouring matters may be used satisfactorily. It is recommended that the grass should be dyed immediately after retting and before spinning, to preserve the characteristic sheen.

The textiles formerly associated with China grass were such articles as handkerchiefs and 'grass cloths,' imported direct from China, but recent efforts to introduce the manufacture as well as the growth of China grass into Europe have led to other developments. Thus at the manufactory of Zittau in Saxony, the fibre has found application in tapestry and dress goods, table-cloths, damasks, lace, fancy knitting yarns, &c. It is also used in the manufacture of incandescent gas-mantles.

A number of other species of *Boehmeria* also supply bast fibres.

CHINA INK *v.* INDIAN INK.

CHINAPHENIN. Trade name for phenetidine-quinine carbonic ester. Formed by treating *p*-phenetidine with phosgene and combining the product with quinine.

CHINA-STONE. A granitic rock, having its felspathic constituent more or less decomposed, but not completely kaolinised, and with an absence of coloured minerals, such as biotite and tourmaline. As the felspar still retains part of its alkali, and as some micaceous mineral is generally present, the stone is fusible; hence it is largely used in the manufacture of porcelain, and when free felspar is not introduced

it forms the only vitrifiable constituent of the paste. China-stone is sometimes known as 'Cornish stone' in consequence of its being largely quarried in Cornwall, where it was discovered by W. Cookworthy, of Plymouth, about 1750. He first noticed it at Tregonning Hill, near Breage, and described it under the local name of 'growan' or 'moor-stone.' It is now obtained principally from the neighbourhood of St. Stephens, near St Austell. In this area it occurs as a local modification of the granite, and is sharply marked off from the normal granite and from the china-clay rock. It is too hard to be worked like the china-clay rock, and has to be blasted and quarried like ordinary granite, in fact it has been used locally as a building stone. The rock requires no preparation, but is sent direct from the quarry to the potteries (For an account of the occurrence of china-stone in Cornwall, *see* Mem. Geol. Survey, Bodmin and St Austell District, 1909; and the Handbook by J. A Howe, quoted below.)

The following commercial varieties are recognised:—

1 'Hard purple,' a hard, white rock with a faint purplish tinge due to the presence of fluor-spar.

2. 'Soft' or 'Mild purple,' similar to the last, but softer.

3 'Dry white stone,' a soft, white variety.

4 'Buff stone,' similar to the last, but iron stained.

The following analyses by W. Pollard and E G Radley are given by J. A. Howe, A Handbook to the Collection of Kaolin, China-clay and China-stone in the Museum of Practical Geology, London, 1914. I. 'Hard purple' china-stone from Goonvean, near St. Stephens; II 'Buff' china-stone from the same locality; III. China-stone from Jersey ('Jersey stone').

	I.	II.	III.
SiO_2	72·28	73·18	77·06
TiO_2	0 05	0 06	0 08
Al_2O_3	14·90	16 13	12·22
Fe_2O_3	0 50	0 52	0·47
MnO	0 01	0·02	0·19
CaO	1·66	0·61	0·16
MgO	0·15	0·14	0·19
K_2O	5·25	4·41	5·07
Na_2O	3·01	2·18	3·23
Li_2O	0 02	0·02	trace ?
H_2O (at 105°)	0·13	0·20	0·39
H_2O (over 105°)	0·68	1·81	0·37
P_2O_5	0·53	0·45	0·25
F	0·88	0·23 FeS_2 0·30	
Cl	0·09	— CO_2 0·04	
	100·07	99·96	100·02

Jersey stone is a decomposed partly kaolinised granite quarried in Jersey. Granite-pegmatite in France; granite-aplite at Meldon, near Okehampton, Devonshire; porphyrite in Saxony; liparite in Japan; and felsite in China are all rocks that are applied for the same purpose.

It has been proposed by J. H. Collins (Hensbarrow Granite District, Truro, 1878) to distinguish china-stone under the name *petunzite*, a word suggested by the Chinese *pe-tun-tse*. In the early part of the 18th century a Jesuit missionary named D'Entrecolles, residing at

King-te-chin, sent to Réaumur, in Paris, samples of the raw materials used in China. These were the first specimens of their kind that had ever reached Europe, and they led to the foundation of the manufacture of porcelain at Sèvres. The china-stone was described by D'Entrecolles as pe-tun-tse, and the china-clay as kaolin ; but it appears that the former name, if not both, must have been erroneously applied. According to the Chinese scholar, Stanislas Julien (Hist. et Fabric. de la Porcel. Chin. Paris, 1856, preface xx.), *pe-tun* signifies ' white paste,' while *tse* is merely a diminutive applied to the material when worked up into small cakes. Hence, pe-tun-se is really the name of small blocks of white clay or prepared paste, and not of the granitic rock. Nevertheless, custom in this country has justified the use of the term *pe-tun-tse* as synonymous with china-stone. L. J. S.

CHINEONAL. Trade name for a compound of quinine and veronal. Used as a hypnotic.

CHINESE BLUE. (*Porzellanblau,* Ger.) Several compounds are sold under this name, of which the following are examples : ultramarine and flake white ; cobalt blue and white lead ; and a double cyanide of iron (Prussian blue) (*v.* PIGMENTS).

CHINESE GREEN or **LOKAO** *v.* LOKAO.

CHINESE LAKE or **SCARLET LAKE** *v.* PIGMENTS.

CHINESE VEGETABLE TALLOW is the hard fat which coats the seeds of the Chinese tallow tree, *Stillingia sebifera* (Willd.), *Stillingia sinensis, Croton sebiferum, Sapium sebiferum,* (Roxb.), *Excœcaria sebifera* (F. Mull), *Carumbium sebiferum*), a tree growing wild in China, and largely cultivated there, as also in Indo-China and the North of India, where the tree thrives luxuriantly. In China the stillingia tree is exploited for both its leaves and seeds. In Tonkin the tree is only cultivated for the sake of its leaves, a decoction of which furnishes a colouring matter used for dyeing silk. In China the fat is only a by-product. The tree commences to produce at the age of 4-5 years, and when it has reached its full development it yields about 24-30 kilos. of seeds a year. The fruit yields about 30 p.c. of a mixture of vegetable tallow and of stillingia oil, half of this quantity consists of vegetable tallow alone, and the other half of stillingia oil, the yield of the latter from the kernels being about 62 p.c. The fruit consists of three oval seeds surrounded by a thick tallow-like mass, the true vegetable tallow. This is recovered by placing the seeds in perforated cylinders and steaming them, so that the fat melts and runs off. Another method is to pass the seeds between fluted rollers, which scrape off the outer fat coating without breaking the seed proper. The scraped-off mass is pressed in the hot primitive wedge presses, and sold under the Chinese name of ' pi-iéou ' or ' pi-yu ' ; it is known in Europe as ' prima ' vegetable tallow. The seeds which have been bared from their fat coating, are then crushed separately and yield the stillingia oil, a drying oil known in China as ' taé-tiéou ' or ' ting-yu.' In another process, the seeds, together with their coating of fat, are crushed, and thus a mixture of vegetable tallow and stillingia oil is obtained. The product

thus prepared is naturally much softer than the true vegetable tallow, and has therefore a lower melting-point and a much higher iodine value. This second quality is sold in Europe as ' secunda ' vegetable tallow, and represents a mixture of ' pi-yu ' and ' ting-yu.' It is sold in China under the name ' mou-iéou.'

The saponification value of commercial samples of vegetable fat varies, therefore, according to the mode of preparation, from 179 to 207. Similarly, the iodine value varies considerably, and numbers ranging from 19 to 32 have been recorded. The composition of vegetable tallow has not yet been definitely ascertained. Stearic acid is absent (Hehner and Mitchell), and it is probable that the fat consists in the main of palmitin and olein.

The oil has an iodine value of about 155, and yields 20 p.c. of an insoluble bromide (m.p. 147°), whereas the fat does not form an insoluble compound with bromine.

Vegetable tallow plays, in China, an important *rôle* as an article of commerce ; it is largely used in the manufacture of candles. During recent years considerable quantities have been exported. The bulk of the vegetable tallow is used in the candle and soap industries. According to Diedrichs (Zeitsch. Nahr. Genussm. 1914, 27, 132) the fat, if properly purified, can be used for food, but soon acquires a bitter taste and unpleasant odour. It is frequently adulterated by the Chinese. J. L.

CHINESE WAX or **INSECT WAX** *v.* WAXES.

CHINESE YELLOW (*King's yellow*) *v.* PIGMENTS.

CHINOCOL. Trade name for a compound of hydroxyquinoline and potassium sulphate ; used as an antiseptic and disinfectant. *v.* CHINOSOL.

CHINOFORM. Trade name for quinine formate.

CHINOLINE *v.* QUINOLINE.

CHINOSOL. Trade name for the potassium salt of 8-hydroxyquinoline-5-sulphonic acid $C_9H_6NOSO_3K,H_2O$, a pale-yellow crystalline powder with a saffron-like smell and a burning taste ; m.p. 175°–177·5° ; readily soluble in water, sparingly soluble in alcohol, insoluble in ether ; with ferric chloride gives an intense green colour, yellowish needles with copper salts, and a white precipitate with barium chloride. Used as an antiseptic. At a concentration of 1 in 1000 its solutions possess as great a bactericidal action as mercuric chloride solutions of the same strength.

CHINOTROPIN. Trade name for urotropine quinate.

CHINOVOSE *v.* CARBOHYDRATES.

CHIOLITE. A double fluoride of aluminium and sodium $3AlF_3,5NaF$, closely akin to cryolite $AlF_3,3NaF$, but crystallising in the tetragonal system. Found at the Ilmen Mountains in the Southern Urals and with crystals in Greenland. L. J. S.

CHIRETTA. *Chirata,* B.P. Is the plant *Swertia chirata* (Buch. Ham.) collected when in flower and dried. Japanese chiretta is *Swertia chinensis* (Franchet). Höhn (Archiv. d. Pharm. 1869, 215) found two bitter constituents in Indian chiretta, viz. chiratin and ophelic acid.

CHITENINE. An oxidation product of

N

quinine, found in the urine after the administration of quinine. Crystallises from dilute alcohol in prisms, m.p. $281° - 282° [a]_D^{17} - 122·6°$.

CHITIN, CHITOSE v. CARBOHYDRATES.

CHLOANTHITE. Native nickel arsenide, $NiAs_2$, isomorphous with smaltite $(CoAs_2)$ (q.v), there being no sharp line of demarcation between the two species. Found as cubic crystals and compact masses at Schneeberg in Saxony and Riechelsdorf in Hesse, where it was formerly mined as an ore of nickel. L. J. S.

CHLORACETIC ACIDS v. HALOGEN ACETIC ACIDS.

CHLORAL Trichloracetaldehyde CCl_3·CHO.
Chloral was first prepared by Liebig, who obtained it by the continuous chlorination of absolute alcohol (Annalen, 1, 189) It was further examined by Dumas (Ann Chim Phys [2] 56, 125), who determined its composition, and by Stadeler (Annalen, 61, 101) Although a chlorinated aldehyde, it cannot be prepared by treating acetaldehyde with chlorine, unless water is present together with calcium carbonate to neutralise the hydrogen chloride formed, since butyric chloral results when dry materials are employed (Pinner, Ber 4, 256).

Industrial preparation. The process by which chloral is manufactured is divided into three stages : the preparation of chloral alcoholate ; conversion of this into chloral , and the formation of chloral hydrate

In a large glass balloon 60 kilos. of alcohol, as completely dehydrated as possible, are subjected to the action of a current of chlorine, the escaping hydrochloric acid being absorbed by water. The introduction of the chlorine lasts a considerable time, in some works 10 to 14 days. At first the balloon must be cooled, for, if the temperature is not properly regulated, the yield is much reduced. After a time the reaction becomes less violent; the mixture is then warmed to 60°, and finally to 100°. When the liquid is completely soluble in water, the current of chlorine is stopped, and on cooling, a white mass of the alcoholate is obtained. In this operation Springmuhl recommends the use of iodine as a chlorine carrier ; Page, the addition of crystallised ferric chloride (Annalen, 1884, 225, 209) ; and in either case the ethyl halide is easily recovered.

In the ordinary process the chlorinated liquid is not allowed to cool, and is transferred to an enamelled still holding 150-200 kilos., where an equal volume of strong sulphuric acid is added in small quantities. The temperature is raised to boiling, the condensed vapours being returned to the still. During the ebullition there is an evolution of hydrochloric acid gas, the cessation of which indicates the termination of the decomposition of the alcoholate. Fractional distillation follows, this ceasing when the thermometer has reached 100°. The distillate is again rectified, the portion coming over above 94° being pure chloral. In some works the final purification is carried out by distilling over chalk or sodium bicarbonate. Ethylene dichloride, ethylidene chloride, and chlorinated ethylene dichloride (b.p. 115°) are also formed as by-products in this reaction (Kramer, Ber. 3, 257).

The chloral is shaken with the theoretical quantity of water and the product of the reaction at once poured over a smooth surface, when it solidifies ; in this state it is sent into commerce. To obtain crystals the warm mass (heat is disengaged in this reaction) is mixed with one-third of its volume of chloroform, and the mixture allowed to cool in closed vessels ; crystallisation is complete in a week. The mother liquors serve for a second crystallisation, and the crystals are dried at the ordinary temperature. Fluckiger (Zeitsch. Chem. [2] 6, 432) recommends crystallisation from warm carbon disulphide or turpentine, and Martius from benzene. Other methods, which have been described, differ from the preceding in that the chlorinated mixture, after solidification and pressure, is sublimed or distilled with calcium chloride (Detsényi, Dingl. poly. J. 209, 224 ; Trillat, J. Pharm. Chim 5, 218).

The following method has been devised for the continuous production of chloral. Chloral and its hydrate are the most volatile products of the action of chlorine on alcohol, and may therefore be removed by continuous distillation. A special apparatus is described ; chlorine and chlorinated alcohol are introduced into a vessel heated in a water-bath, from which the vapours pass into a second and then into a third heated vessel. The residual chlorine is absorbed in a cylinder provided with baffle plates. The rectifier, which also acts continuously, is provided with baffle plates ; it is fed at the middle with chloral, and at the top with sulphuric acid (66° B.). The final rectification is carried out as already described. The same apparatus may be used for converting chloral into chloroform (Besson, Eng. Pat. 17202 ; U.S. Pat. 774151 ; J. Soc. Chem. Ind 1901, 1139)

Chloral is formed when ethyl alcohol is allowed to drop into the anode compartment of a cell in which an alkaline chloride is being electrolysed.

Theories to explain the action of chlorine on alcohol and the subsequent production of chloral have been proposed by Lieben (Ber. 3, 910); Wurtz and Vogt (Compt. rend. 74, 777) ; Jacobsen (Ber 15, 601) ; and Brochet (Bull. Soc. chim. 17, [3] 228).

Chloral is a colourless pungent liquid, which solidifies at $-75°$ (Berthelot, Ann. Chim. Phys.[5], 12, 536), at $-57·5°$ (Van Rossem. Zeitsch. physikal. Chem. 1908, 62, 681); and is readily soluble in water, alcohol, and ether. Its b.p. is $97·7°$ (corr.) and sp gr. $1·54175$ at 0° (Passavant, Chem. Soc. Trans. 39, 55 ; Thorpe, ibid 37, 191); b.p. $96°-97°$ at 750 mm., and sp.gr. $1·5121$ at $20°/4°$ (Brühl, Annalen, 203, 11) ; b.p. 97° at 740 mm. (Van Rossem, l.c.). Three hydrates exist : (1) a semihydrate $2C_2HCl_3O,H_2O$; true m.p. is about 49°, the highest observed 80° ; (2) the ordinary monohydrate existing in two pseudo-symmetrical modifications ; true m.p. $47·4°$, highest observed 54° ; (3) a heptahydrate, m p. $-14°$ (Pope, Chem. Soc. Proc. 1896, 142 ; and Van Rossem, l.c.). According to Wolf (J. Phys. Chem. 4, 21) ; there is only one modification, the difference in melting-points being due to dissociation. Nascent hydrogen reduces it to aldehyde (Personne, Annalen, 157, 113), which it closely resembles in reducing ammoniacal silver nitrate solution (Stadeler, Annalen, 106, 253), and in forming crystalline compounds with sodium

disulphite (*ibid*).; with ammonia (*v.* chloral ammonium); with hydrogen cyanide (Bischoff and Pinner, Ber. 5, 113; Annalen, 179, 77); with amides (Wallach, Ber. 5, 251; Sulzberg, D.R.P. 198715; J. Soc. Chem. Ind. 1908, 958); and with amines (Wallach, *l.c.*; Rügheimer, Ber. 1906, 1653; Wheeler, Amer. Chem. J. 1902, 1063, 1908, 136; 1909, 937)

When heated with aqueous alkalis it decomposes into chloroform and an alkaline formate, and a similar reaction occurs when alcoholic potash or soda is employed (Kekulé, Annalen, 119, 188). Chlorine, bromine, or iodine and aluminium chloride convert chloral into hexachlorethane (Mouneyrat, Bull. Soc. chim. 17, [3] 796). Fuming nitric acid converts it into trichloracetic acid, and, according to Grabowski (Ber 6, 225), fuming sulphuric acid combines with it in the cold, but on heating converts it into chloralide $C_8H_4Cl_6O_4$ (compare Grabowski, Ber. 8, 1433; Städeler, Annalen, 61, 114; Wallach, *ibid.* 193, 1). Chloral condenses with succinic acid by means of acetic anhydride to form trichloromethylbaraconic acid (Fittig and Miller, *ibid.* 255, 43).

Derivatives. **Chloral ammonium** $C_2H_4Cl_3NO$ is prepared by the action of ammonia on a solution of chloral in chloroform (Schiff, Ber. 10, 167). It is a white crystalline solid, resembling chloral hydrate in taste and colour; it melts at 64°, and is slightly soluble in water, more readily soluble in alcohol (Personne, Annalen, 157, 113; Compt. rend. 71, 228) Nesbit recommends the use of chloral ammonium instead of urethane and chloral hydrate, since the action of chloral hydrate on the respiration centres and the heart is retarded by the introduction into that compound of an amino- group (J. Soc Chem Ind. 1889, 113; 1890, 889) By heating chloral ammonium on the water-bath, chloroform and ammonia distil off, and the residue consists of formamide and *chloralimide* $C_2H_2Cl_3N$, the latter of which is extracted with alcohol. *Isochloralimide* is also formed, and according to Schiff (Gazz chim. ital. 21, 490), dimolecular and trimolecular -imides exist Chloralimide can also be prepared by heating chloral and chloral ammonium until chloroform is no longer evolved, and by the reaction between chloral hydrate and ammonium acetate (Schiff, *l.c.*; Pinner and Fuchs, Ber 10, 1068; Arends, Chem. Ind. 16, 78; Béhal and Choaz, Compt rend. 109, 817; 110, 1270). It has remarkable antipyretic and analgesic properties. Other chloralimido compounds have been described by Moschelles (Ber. 24, 1803)

Chloralamide or **chloral formamide** $C_3H_4Cl_3NO_2$ is produced by gently heating chloral and formamide in molecular proportions (J. F. von Mering, Eng. Pat. 7391; D. R. P. 50586; J. Soc. Chem. Ind. 1890, 413). When recrystallised, it forms colourless crystals melting at 115°-116°; it is soluble in 9 parts of water, or in 1½ parts of 96 p.c. alcohol. It is without smell, and has a slightly bitter taste; when heated above 60°, it is decomposed; aqueous or alcoholic solutions are unaffected by weak acids or by silver nitrate, but are rapidly decomposed by alkali hydroxides, more slowly by alkali carbonates. As a hypnotic it has been proved superior to chloral hydrate, and is of most value in cases of nervous insomnia and similar disorders (Hagner and Hübner),

Weiner Med. Presse, 1899, 1361). It has no corroding action, does not affect the digestion, nor disturb the heart. It may be taken internally as a powder, prepared by triturating 1-3 grams of the amide with 1 gram of fennel-oil sugar (*Ellæosaccharum Fœniculi*) (Merck's Bull. 1889, 85).

Chloralose $C_8H_{11}Cl_3O_6$ is obtained by heating equal parts of chloral and glucose, on the water-bath. The vitreous mass is boiled with water to remove the chloral, and the concentrated aqueous solution deposits a crystalline compound, from which chloralose is extracted by alcohol. On treating the residue with ether, a compound isomeric with chloralose, termed *parachloralose*, is obtained. Chloralose melts at 187°, and is a powerful hypnotic; whilst parachloralose melts at 227°, and possesses no hypnotic properties. By oxidising these compounds with nitric acid, followed by potassium permanganate, the corresponding chloralic acids are obtained; m.p. 212° and 202° respectively (Hanriot and Richet, Bull. Soc. chim. [3] 11, 37; 12, 303; Compt. rend. 116, 63; 122, 1127; 148, 1265; Meunier, *ibid.* 122, 142; Petit and Polonovski, Bull. Soc. chim. 3, [3] 861).

Chloral-acetonechloroform $C_6H_8O_2Cl_6$ is prepared by heating molecular quantities of chloral and acetonechloroform. It melts at 65°, and has a faint odour and taste resembling camphor (Hoffmann-Laroche, U.S. Pat. 778277; J. Soc. Chem. Ind. 1905, 150).

Chloral-bromal-carbamide is obtained by mixing urea with molecular quantities of chloral and bromal, or equivalent quantities of their hydrates in the presence of concentrated hydrochloric or sulphuric acid (Kalle & Co. D. R. P. 128462; Chem. Zentr 1902, 1. 547). Chloral hydrate in saturated aqueous solution combines with urotropine and caffeine, forming in each case two compounds according to the proportions of the reagents employed.

Monochloralurotropine,$C_6H_{12}N_4C_2HOCl_3,H_2O$, crystallising in rhombohedra, and *dichloralurotropine*, $C_6H_{12}N_4(C_2HOCl_3,H_2O)_2$, crystallising in needles, resemble one another in their properties. They are colourless and odourless, and very soluble in alcohol and water. They volatilise at about 100° without melting. They are both neutral substances, which reduce copper solutions and ammoniacal silver nitrate. With mineral acids they yield formaldehyde, and with alkalis the chloral is attacked, giving chloroform in the cold and carbylamine on heating.

Dichloralcaffeine,

$$C_8H_{10}O_2N_4,H_2O,(C_2HOCl_3,H_2)_2,$$
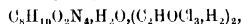
m.p. 72°-73°, slowly loses 1 mol. of chloral and passes into *monochloral caffeine*, $C_8H_{10}O_2N_4, H_2O,(C_2HOCl_3,H_2O$, m.p. 92°-93°. The latter compound dissolves in water, and in solution slowly dissociates, the caffeine separating out. In hot alcoholic solution it is completely dissociated. When heated at 100° all the chloral is driven off, leaving pure caffeine (Leulier, J. Pharm. Chim. 1912 [vii.] 6, 18).

The following condensation products of chloral have been prepared: chloralacetone, chloralacetophenone, and chloraldol (Gigli, Gazz. chim. ital. 28, [2] 83; Königs, Ber. 1892, 792; 1893, 554; Wislicenus, Kircheisen, and Sattler,

ibid. 1893, 908) ; carbonylchloraldehydes (Farb. vorm. F. Bayer & Co. D. R. P. 121223, Chem. Zentr. 1901, ii. 69) ; chloral nitrite (Bertoni, Gazz. chim. ital. 24, ii. 20) ; the compounds with aminoazobenzene (Betti, *ibid.* 28, 241) ; with amidooxybenzoic esters (Kalle & Co. D. R. P. 112216 ; Chem. Zentr. 1900, ii. 791) ; with aromatic hydrocarbons (Biltz, Ber 1893, 1952 ; Dinesmann, Compt. rend. 1905. 141, 201) ; with hexamethylenetetramine (Lederer, Eng. Pat. 17693 ; J. Soc. Chem. Ind 1897, 1039) ; with hydroveratine (Frankforter, Amer. Chem. J. 20, 358) ; with methylpropanoldialkamino- acids (Poulenc Frères & Fourneau, Fr Pat. 382787 ; D R. P. 203643 ; J. Soc Chem. Ind. 1908, 246) , with menthol and terpinol (Wagnitz, Eng. Pat. 19103 ; J. Soc Chem Ind. 1899, 856 ; Schmitt, Compt. rend. Soc. Biol. 1890, 678) ; and with resorcinol (Causse, Bull. Soc. chim. 3, [3] 861 ; Hewitt and Pope, Chem. Soc. Trans. 1896, 1265).

Polymerides. Two polymerides of chloral are known, an insoluble and a soluble substance. When pure, chloral is perfectly stable, but traces of impurities, and particularly of sulphuric acid (Byasson, Compt. rend 91, 1071) convert it into *metachloral*, a white amorphous solid It may be prepared by leaving chloral hydrate in contact with half its weight of concentrated sulphuric acid for several hours, until a pasty mass is formed. After pouring off the acid, the residue is introduced into a well-cooled solution of hydrochloric acid, and the product, which now becomes solid, is washed and dried over sulphuric acid. Chloral alcoholate may be substituted for chloral hydrate in this preparation (Gartner, D. R. P. 170534 ; Chem. Soc. Abstr. 1906, 1 628). Another method is to add 7 parts of anhydrous aluminium chloride to 100 parts of well-cooled anhydrous chloral, the temperature being kept below 40°. In the course of an hour the whole mass solidifies After 24 hours the hard mass is broken up, extracted with dilute hydrochloric acid, washed with alcohol, and dried at a moderate temperature (Erdmann, D R. P. 139392 ; Chem Zeit 27, [20]223). It is insoluble in alcohol, ether, water, and acids, but soluble in sodium carbonate solution. On warming with alcohol, it yields chloroform, and on distillation at 180°–250° is reconverted into chloral (Kolbe, Annalen, 54, 183 [footnote]). It is tasteless, and can be employed as an anæsthetic ; unlike chloral hydrate, it has no irritating effect on the mucous membrane of the stomach.

The soluble polymeride is obtained by treating chloral with pyridine or any other amine in the cold, and then acidifying. It is a slightly volatile anæsthetic substance, volatilising without melting, converted by hot water or hot alcohol into chloral hydrate and chloral alcoholate respectively, and decomposed by alkalis into chloroform and formic acid. It is soluble in water (Gartner, D. R. P. 165984 ; U.S. Pat. 768744 ; Chem Soc. Abstr 1906, 1. 481).

Chloral hydrate $CCl_3 \cdot CHO + H_2O$ or $CCl_3 \cdot CH(OH)_2$.

Properties.—Chloral hydrate crystallises in monoclinic tables (Groth, Ber. 5, 676), and has a peculiar odour and sharp taste. Its m.p. is 57° (Meyer and Dulk, Annalen, 171, 75),

47·4° (Van Rossem, Zeitsch. physikal. Chem. 1908, 62, 681) ; b.p. 97·5° ; and sp.gr. 1·818 (in powder) and 1·848 (crystallised) (Schröder, Ber. 12, 562). It dissolves readily in water, 1 part of water dissolving 4·7 parts of chloral hydrate at 17·5° (Mauch, Arch. Pharm. 240, 113), alcohol, ether, chloroform, turpentine, and light petroleum ; and its solubility in carbon disulphide is given by Fluckiger (*l.c.*) as 1 in 45 at 15°–18°, and 1 in 4·5 at the boiling-point. Concentrated sulphuric acid decomposes it into chloral and water, and alkalis act upon it as upon chloral. A modification of the hydrate, melting at 80°, is obtained by rapidly evaporating an acetic acid solution of anhydrous chloral over sulphuric acid (Meyer and Dulk, *l.c.*) ; this is probably the semihydrate described by Van Rossem (*l.c.*). Under the influence of light and air, chloral hydrate is decomposed, the decomposition products being hydrochloric acid and carbon dioxide or monoxide, or water, chlorine, and carbon dioxide, the amount of available oxygen determining the products (School and Van den Berg. Ph Weekblad. 43, 42)

Chloral hydrate should be free from alcoholate, which has not the same physiological properties, and when warmed with twice its volume of water it should give a clear solution, free from oily drops and not precipitated by silver nitrate. When carefully heated, it should volatilise completely, and the vapours should not be inflammable ; when gently warmed with 3 vols. of strong sulphuric acid the mixture should remain clear. On warming chloral hydrate with potassium hydroxide, turbidity is caused through the separation of chloroform , the clear portion is decanted, and iodine dissolved in potassium iodide added. So soon as the liquid begins to turn yellow, it is cooled, when the presence of alcohol and consequently of chloral alcoholate, is indicated by the formation of a precipitate of iodoform (Trillat, J. Pharm. Chim. 5, 218). Chloral alcoholate may also be detected by the Zeisel method for the estimation of ethoxyl (Schmidinge, Monatsh 21, 36). Chloral hydrate is converted into alcoholate when dissolved in alcohol, and similarly, chloral alcoholate is very slightly soluble in water, dissolving slowly to form chloral hydrate. Potassium carbonate is a good antidote to chloral poisoning, if it has not reached the blood (Klar, J. Soc Chem. Ind. 1896, 555).

Physiological Action.—Compare Liebreich (Ber. 2, 269) ; Personne (Compt. rend. 78, 129) ; Byasson (*ibid.* 78, 649) ; Tomaszewicz (abstracted, Chem. Soc. Trans. 1874, 814) ; Tanret (J Pharm Chim. [4] 20, 355) ; and Trillat (*l.c.*). Mering, Zeitsch. physiol. Chem. 6, 1882, 480. According to the last-named authority is reduced to trichlorethyl alcohol ($CCl_3 \cdot CH_2 \cdot OH$) in the body and not into chloroform, as suggested by Liebreich, who first proposed its use as an hypnotic.

Estimation.—4 grams of the sample are treated with 30 c.c. of normal caustic soda in a stoppered bottle, and shaken vigorously for a few minutes without the application of heat. On titrating back with normal sulphuric acid, using litmus as an indicator, 5·8 c.c. should be required for complete neutralisation (Alcock and Thomas, Pharm. J. 63, 236 ; and Sargeant, *ibid.*). Owing to the secondary reaction $CHCl_3 + 3NaOH = 3NaCl + CO + 2H_2O$, this titration with acid is

slightly inaccurate. Modifications of the method have been devised by Trillat (*l.c.*); Hinrichs (Pharm. J. 70, 530); Deagrez (Compt. rend. 125, 780; Analyst, 23, 76); Self (Pharm. J. 79, 4); and Garnier (Chem. Zentr. 1908, i. 1492). Another method is to heat 0·3 gram of the sample with 1 gram of aluminium powder, or 2·5 grams of zinc filings, 15 c.c. of glacial acetic acid, and 40 c.c. of water under a reflux condenser for half an hour. The mixture is filtered and washed, and the chlorine estimated volumetrically or gravimetrically as silver chloride (Self, *l.c.*). Wallis (Pharm. J. 76, 162) treats the chloral hydrate with caustic soda in a bottle, and then estimates the chlorine as silver chloride. It may also be determined iodometrically (Rupp, Arch. Pharm. 241, [5] 326).

Chloral hydrate may be detected by means of the green colour formed on the addition of antimony trichloride to a solution in castor oil (Covelli, Chem. Zeit. 31, 342); or by the colours formed when it reacts with resorcinol in the presence of sulphuric acid (Jaworowski, Zeitsch. anal. Chem 37, 60). Another method is to add a solution of ammonium sulphide, when a pinkish or yellow precipitate is obtained, and an oil having the odour of walnuts (Lesinsky and Grundlich, Amer Chem. J. 19, 603). It may also be detected by the reducing action of the formic acid into which it may be converted In presence of compounds containing the CCl_3 group, *e.g.* chloroform and trichloracetic acid, the substance dissolved in water and slightly acidulated with sulphuric acid is treated with zinc in the cold When the evolution of hydrogen has ceased, a strip of filter paper, soaked in a solution of sodium nitroprusside and 5 p.c piperidine solution is hung over the liquid, which is gently warmed, when the acetaldehyde formed colours the paper blue. 1 part of chloral hydrate in 20,000 may thus be detected (Jona, Giorn. Farm. Chem. 1912, 61, 57). Chloral hydrate is valuable for extracting alkaloids from plants containing much resin, essential oils, &c. (Schaer, Zeitsch. anal. Chem. 37, 469); it is used in rubber analysis (Weber, J. Soc. Chem. Ind. 1903, 576); in microchemical investigations (Schaer, Chem Soc. Abst. 1908, i. 62); and in qualitative analysis (Mauch, Arch. Pharm. 240, 166).

Derivatives.—**Chloral antipyrine** is obtained by the condensation of chloral hydrate with antipyrine (Béthal and Choaz, Ann. Chim. Phys. 27, 319).

Chloral caffeine is formed when chloral hydrate and caffeine are brought together in aqueous or alcoholic solutions in molecular proportions. It is recrystallised from warm water at 30°, and, owing to its easy solubility as opposed to the difficult solubility of caffeine, is of medicinal value (Chem. Fab. auf Act. vorm E. Schering, D. R. P. 75847; J. Soc. Chem. Ind. 1895, 987).

Chloral tannin is prepared by the condensation of chloral hydrate with tannin in the presence of sulphuric acid. It is a greyish-brown amorphous powder, having valuable dermatological properties (Farb. vorm. Fried. Bayer & Co. D. R. P. 98273; Eng. Pat. 2882; J. Soc. Chem. Ind. 1899, 172).

Chloraldoxime is prepared by treating chloral hydrate (1 mol.) with hydroxylamine hydrochloride (4 mols.) and a little water; m.p.

39°-40° (Meyer, Annalen, 264, 116; Tarugi, Gazz. chim. ital. 21, ii. 6).

Chloralhydroxylamine is obtained by triturating molecular quantities of chloral hydrate, sodium carbonate, and hydroxylamine hydrochloride, dissolving the mass in a little water, and extracting with ether; m.p. 98° (Hantzsch, Ber. 1892, 701).

Compounds with formaldehyde are described by Pinner (Ber. 1898, 1926).

Chloral alcoholates. The preparation of *chloral ethylalcoholate* has already been described. It may also be obtained by the action of chloral on absolute alcohol (Martius and Mendelssohn, Ber. 3, 444). It crystallises in needles, melts at 44°-46° (Meyer and Dulk, Annalen, 171, 78), at 46° (Lieben, Ber. 3, 907); boils at 115°; is sparingly soluble in water, more soluble in absolute alcohol, 1 part of alcohol dissolving 4·4 parts of chloral alcoholate at 17·5° (Mauch, Arch. Pharm. 240, 113). Sulphuric acid decomposes it into chloral and alcohol Chloral propylalcoholate, b p. 120°-122°, and chloral isopropylalcoholate, m p. 47°, and b.p. 108°, have been described by Gabutti (Gazz. chim. ital. 31, i. 86), and Vitoria (Chem. Soc. Abst. 1905, i. 110); chloral amylalcoholate by Gadamer (Arch. Pharm. 243, 30), and Kalle & Co. (D. R. P. 115251; Chem. Zentr. 1900, ii. 1141). Other alcoholates have been prepared by Jacobsen (Annalen, 157, 224), and Kuntze (Arch. Pharm. 246, 91).

Butyl chloral $CH_3·CHCl·CCl_2·CHO$; more correctly, tri-chlor-butyric-aldehyde; b.p. 164°-165° at 750 mm.; sp gr. 1·3956 at 20°/4° (Brühl, Annalen, 203, 20). It is a colourless oil, having a characteristic chloral odour, formed by the action of chlorine upon ordinary aldehyde or paraldehyde (Kramer and Pinner, Ber. 3, 383). Chloracetaldehyde $CH·CClCHO$ is first formed, and this condenses with another molecule of acetaldehyde, forming a-chlorcrotonaldehyde $CH_3·CH:CCl·CHO$ and water, and this, by the action of more chlorine, forms the butyl chloral.

Preparation.— Chlorine is led through cooled paraldehyde (or aldehyde cooled by a freezing mixture); water is then added, and the liquid neutralised with calcium carbonate. The mixture is then distilled on the oil-bath in a current of steam, and the hydrate is thus obtained. This is then purified by recrystallisation from water, and decomposed by distillation in a stream of hydrochloric acid gas (Pinner, Annalen, 179, 26).

Butyl chloral is converted by fuming nitric acid into aaβ-trichlorbutyric acid. Phosphorus pentachloride converts it into a body $C_4H_4Cl_4$, which boils at 200°. It combines with zinc-ethyl to form a compound which is decomposed by water with formation of trichlorobutyl alcohol.

The ammonia compound

$$CH_3·CHCl·CCl_2·CH(OH)NH_2$$
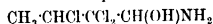
m.p. 62°, is formed by leading ammonia into a cooled mixture of 1 part of butylchloral, and 1½ parts of chloroform (Schiff and Tassinari, Ber. 10, 1783). It forms a solid mass, insoluble in water, soluble in ether, alcohol, and chloroform. Is readily decomposed on heating.

Butyl chloral has a strong affinity for water, and readily forms

Butylchloral hydrate $CH_3 \cdot CHCl \cdot CCl_2 \cdot CHO$ $+H_2O$. This compound, which is also known as butyl chloral, is prepared by passing chlorine into paracetaldehyde (Freundler, Compt. rend. 143, 682). It forms white crystalline trimetric plates of a peculiar odour, with difficulty soluble in cold, more readily in hot water; very readily soluble in alcohol; m.p. 78°, with partial dissociation, and sp.gr. 1·694 (Schröder, Ber. 12, 562). For some years after its discovery in 1870, it was regarded as croton-chloralhydrate. It is decomposed by distillation into the chloral and water. Alcohol and potassium cyanide convert the hydrate into ethyl α-chlorcrotonate. Zinc and hydrochloric acid, or zinc-dust and water, produce mono-chlor-crotonaldehyde, and finally crotonaldehyde (Sarnow, Annalen, 164, 108). With acetic acid and iron filings, butyraldehyde, normal butyl alcohol, and crotonyl alcohol are produced (Lieben and Zeisel, Monatsh. 1, 840) It is a valuable anodyne in cases of neuralgia, facial rheumatism, periostitis, &c. The following composition is recommended: butyl chloral hydrate, 2–5 grams; alcohol, 10 grams; glycerol, 20 grams, and distilled water, 120 grams (J Soc Chem Ind. 1889, 476; 1890, 889). It is frequently adulterated with the cheaper chloral hydrate, from which it may be distinguished by the following reaction: A solution of pyrogallol in pure 65 p.c. sulphuric acid gives, when gently and carefully warmed, a blue colour with chloral, a ruby colour with butyl chloral and a more or less violet-to-blue colour with mixtures of the two compounds. On addition of a large quantity of water, the blue colour obtained with chloral changes to yellowish-brown, and the ruby colour obtained with butyl chloral to a more or less deep-violet colour (Galbutti, J Soc. Chem. Ind. 1894, 273).

Derivatives.—Butylchloralantipyrine, yellow crystals, m.p 70°–71° (Calderato, Chem Zentr 1902, ii. 1387); butylchloraldoxime (Tarugi, Gazz. chim ital. 21, ii. 6).

CHLORALAMIDE. Syn for chloral form-amide $CCl_3 - CH \cdot NH \cdot CHO$ used as a hypnotic

$$\underset{\mathrm{OH}}{|}$$

and sedative.

CHLORALUM *v.* DISINFECTANTS.

CHLORAMINE-BLUE, -GREEN, *v.* AZO-COLOURING MATTERS.

CHLORAMINE-T. (Sodium-*p* toluenesulphochloramide $CH_3C_6H_4SO_2NNaCl$), first obtained by Chattaway (Chem. Soc Trans. 1905, 87, 153), has been shown by Dakin to be a valuable antiseptic in military surgery for the treatment of infected wounds, and has been employed in cases of cerebrospinal meningitis; diphtheria, &c. It may be obtained from *p*-toluene sulphonic chloride, a by-product in the manufacture of saccharin (*q.v.*); or, directly, from toluene by sulphonation and transformation of the sodium salt into the sulphonic chloride by the action of phosphorus pentachloride or a mixture of the pentachloride and phosphoryl chloride, and conversion of the sulphonic chloride into sulphonamide by treatment with ammonia or ammonium carbonate. To convert the amide to chloramine, one molecular proportion is dissolved in a warm strongly alkaline solution of sodium hypochlorite (1·3 to

2·0 N strength), when on cooling the greater part of the chloramine separates out, and the remainder can be obtained by evaporation. It is important to have an excess of caustic soda: for each mol. of amide about 1·05 to 1·1 mols. of hypochlorite and 1 mol. of sodium hydroxide. Known also as *chlorazene* and *tolamine*.

Dichloramine T, toluene-*p*-sulphodichloramide $CH_3C_6H_4SO_2NCl_2$, is also employed as an antiseptic. It is prepared by dissolving *p*-toluenesulphonamide in bleaching powder solution or by acting on chloramine T by hypochlorous acid. Insoluble in water but dissolves in chlorinated paraffin or chlorinated eucalyptol which is then diluted with paraffin oil.

The persistent odour which clings to the hands after immersion in hypochlorite solutions appears to be due to protein chloramine combinations (Briggs).

CHLORAMINE-YELLOW *v.* PRIMULINE AND ITS DERIVATIVES

CHLORANIL *v* QUINONES.

CHLORATE OF POTASH, SODA *v* CHLORINE.

CHLORAZENE. Syn. for Chloramine T. (*q.v*).

CHLORAZIDE. N_3Cl A gas obtained by mixing solutions of sodium azide N_3Na, and sodium hypochlorite, and acidifying with acetic acid Chlorazide is highly explosive, slightly soluble in water, and insoluble in caustic alkalis (Raschig, Ber. 1908, 4194).

CHLORAZOL-BROWN, -DEEP BROWN, -BLUE, -VIOLET *v* AZO- COLOURING MATTERS.

CHLORENE ($C_{46}H_{26}$) A green hydrocarbon obtained together with decacylene and fluorocyclone by heating acenaphthene with lead oxide at 350° and extracting with benzene and light petroleum in the cold. It crystallises in small dark green scales Dilute solutions are pure deep green in colour but become brownish-red on exposure to sunlight Concentrated solutions appear purple-red by a bright transmitted light (Dziewonski and Suknarowski, Ber. 1918, 51, 457).

CHLORETONE *v* ACETONECHLOROFORM.

CHLORIDE OF LIME, POTASH, SODA *v.* CHLORINE.

CHLORINE. Symbol Cl. At. wt. 35·46. HISTORICAL Chlorine was first obtained by Scheele in 1774 by the action of hydrochloric acid upon manganese dioxide, and was termed by him 'dephlogisticated marine acid air.' In 1785 Berthollet suggested its use for bleaching vegetable fibres, and this application continued until 1789, when this very objectionable gas, and its equally objectionable aqueous solution, were replaced by an unobjectionable solution prepared by dissolving the gas in an alkali; the hypochlorites so prepared have been used for bleaching from then to this day.

The idea that it was a compound substance prevailed until 1809, when Gay-Lussac and Thénard suggested that it was probably an elementary body, a supposition confirmed by the investigations of Davy in 1810 (Phil. Trans. 1811, 1, 32). Davy gave it its present name, from χλωρός, greenish-yellow, in allusion to its characteristic colour.

OCCURRENCE. Chlorine is never found free in nature; it always occurs combined with metallic elements. Sodium chloride occurs to

the extent of 3 p.c. in sea-water, and as *rock salt* in large quantities in Galicia, Tyrol, Transylvania, Spain, and in England (particularly in Cheshire) (*v. Sodium Chloride,* art. SODIUM). Potassium chloride is found as *sylvine* (*q.v.*), and in association with magnesium chloride as *carnallite* $KCl\cdot MgCl_2,6H_2O$ (*q.v.*) in the salt-beds of Stassfurt, and in a few parts of North France, and in sea-water. Other naturally occurring chlorides are *matlockite* $PbCl_2\cdot PbO,$ *horn silver* AgCl, *atacamite* $Cu_2Cl(OH)_3,$ *calomel* HgCl, &c. Ferric chloride Fe_2Cl_6 and sal ammoniac are occasionally found native as products of volcanic action. Magnesium chloride is found in considerable quantity in sea-water and in many natural waters. Calcium chloride is found in certain brines.

Sodium and potassium chlorides are present in most animal secretions, and free hydrochloric acid is met with in the gastric juice. Many plants, growing in proximity to the sea, and many inland plants contain notable quantities of chlorides

PREPARATION FOR LABORATORY PURPOSES The oldest mode of preparing chlorine for laboratory purposes consists in heating manganese dioxide with hydrochloric acid, or by heating a mixture of manganese dioxide, common salt, and sulphuric acid :

$$MnO_2+4HCl=Cl_2+MnCl_2+2H_2O$$
$$2NaCl+MnO_2+3H_2SO_4$$
$$=Cl_2+2NaHSO_4+MnSO_4+2H_2O$$
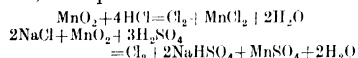
It is readily prepared by slowly dropping a clear strong solution of bleaching powder into concentrated hydrochloric acid Bleaching powder made commercially into small cubes may be used in a Kipps' gas generator containing strong hydrochloric acid If required in rather large quantity it is most easily obtained from liquid chlorine supplied commercially in steel cylinders.

PROPERTIES OF CHLORINE. • At ordinary temperatures and pressures chlorine is a greenish-yellow gas, which becomes darker in colour as it is warmed ; under strong pressures the colour becomes orange-yellow ; its absorption spectrum shows numerous dark lines in addition to complete absorption in the blue and violet. Even when largely diluted with air, the gas possesses a characteristic pungent and irritating smell ; it rapidly attacks the nasal and lung membranes, and in such cases the best relief is obtained by breathing alcohol vapour or a little chloroform vapour and keeping in a warm room.

The sp.gr. of chlorine gas shows a gradual diminution up to 240°, when its density becomes normal, viz. 2·4502 (Jahns, Ber. 15, 1242).

40°	80°	120°	160°	200°	240°
2·4844	2·4776	2·4708	2·4641	2·4572	2·4504

By the application of either suitably increased pressure, or of a suitable low temperature, chlorine gas is readily liquefied to a dark greenish-yellow liquid of sp.gr. 1·33, b.p. −34·5°. The critical temperature is 144·0°, the critical pressure 76·1 atm., and the critical density 0·573. The density of liquid chlorine may be represented by the formula :

$$d_t=0·687014+0·0002379(144-t)$$
$$+0·0622109\sqrt{144-t}$$

The ratio of the critical density, to that calculated from the simple gas laws is 3·635, and the value of Trouton's constant, that is the quotient of molecular heat of evaporation and the absolute temperature of the boiling-point, is 20·67, indicating that chlorine behaves as a normal substance. The specific heat between 0° and 24° is 0·2262, and the heat of evaporation at 8° is 62·7. The vapour tension is in atmospheres :

at −40°	.	.	.	0·74
− 20°	.	.	.	1·84
0°	.	.	.	3·66
+20°	.	.	.	6·62
40°	.	.	.	11·50

It can be solidified at a low temperature. Liquid chlorine is not miscible with water ; its refractive index is lower than that of water, and it is a non-conductor of electricity.

Chlorine gas is readily soluble in water, its absorption coefficient between 10° and 41·5°, according to Schönfeld (Annalen, 93, 26 ; 96, 8), is

$$3·0361-0·046196t+0·0001107t^2$$

by means of which the following table showing the volume of chlorine at 0° and 760 mm. absorbed by 1 vol of water at varying temperatures from pure chlorine gas having a pressure of 760 mm is calculated :

10°	15°	20°	25°	30°	35°
2·5852	2·3681	2·1565	1·9504	1·7499	1·5550

(*v.* also Pickering, Chem. Soc. Trans. 1880, 139).

The volume of chlorine absorbed from a mixture of that gas with an indifferent gas, as hydrogen or carbon dioxide, is greater than that calculated from the law of partial pressures (Roscoe, Chem. Soc. Trans. 8, 14).

Chlorine-water has the characteristic smell and colour of the gas ; in daylight, and especially when exposed to sunshine, it gradually loses its colour owing to the action of the chlorine on the water, the main reaction being

$$H_2O+Cl_2=2HCl+O$$
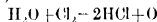
CHLORINE HYDRATE A solution of chlorine in water below 9° deposits crystals of so-called chlorine hydrate of a light-yellow colour, which become almost white when cooled to 50°. By gently heating the crystals in a sealed tube, they are readily resolved into water and free chlorine, which may be thus obtained as a liquid.

GENERAL CHEMICAL PROPERTIES.—Chlorine is an active chemical agent, and combines with many of the elements even at the ordinary temperature. Phosphorus ignites spontaneously in the gas, forming phosphorus trichloride. Finely divided arsenic, antimony, copper, tin, lead, and iron burn in chlorine, forming the respective chlorides, but most of these metals, when presented in bulk, behave quite differently, as the trace of solid chloride formed acts as an impervious layer and the reaction can proceed no further ; but metallic tin forming a liquid chloride $SnCl_4$ is entirely converted into that chloride. Chlorine and hydrogen may be mixed together in the dark without combining, but such mixtures explode violently in bright daylight or when heated. During any of the above acts of combination much heat is evolved.

Certain of these reactions are modified if the chlorine is absolutely free from moisture. Wanklyn (Chem. News, 20, 271) found that sodium might be melted in dry chlorine without action, although the metal readily burns in chlorine as ordinarily prepared. Cowper (Chem. Soc. Trans. 43, 153) found that Dutch metal, zinc, and magnesium were unacted upon by dry chlorine; silver and bismuth were only slowly attacked. The indifference of dry chlorine to steel and brass enables liquid chlorine to be manufactured and shipped in vessels made of those metals.

With many inorganic chemical compounds chlorine also combines directly, thus it unites with sulphur dioxide, carbon monoxide, phosphorus trichloride, ferrous chloride, stannous chloride.

With very many organic non-saturated compounds chlorine also combines directly, e.g. with ethylene, acetylene, and benzene (under certain circumstances), and additive compounds are formed; in the case of acetylene the reaction is so energetic that it becomes explosive; lignocellulose also readily combines with chlorine.

With saturated organic compounds as marsh gas and the paraffins, acetic acid, alcohol, &c., chlorine forms one or more substitution products, and the eliminated hydrogen is simultaneously converted into hydrochloric acid.

With such organic compounds as benzene and toluene, chlorine may react either to form addition or substitution products, or both simultaneously, and such reactions are largely influenced by the temperature and by the presence of other substances as ferrous chloride, iodine, &c.

With turpentine chlorine reacts so readily that the oil inflames spontaneously, and much of it is totally destroyed with the production of free carbon and hydrochloric acid

In presence of water chlorine acts on many substances, both inorganic and organic, as a powerful oxidising agent, and these reactions may be explained by the assumption that the mixture reacts to a small extent to form hypochlorous acid, that is $HOH + Cl_2 = HOCl + HCl$; hypochlorous acid is an intensely active substance, capable of converting manganous oxide into permanganic acid, chromium trioxide into chromic acid. The oxidising action of chlorine and water often becomes more energetic in the presence of bases. In this way monoxide of lead may be converted into dioxide, manganous oxide into manganese dioxide, sulphur into sulphuric acid, ferrocyanides into ferricyanides, manganates into permanganates, and many organic substances and colouring matters may be more or less completely oxidised.

INDUSTRIAL PREPARATION OF CHLORINE.

Chlorine gas has been prepared on the small industrial scale by the addition of strong sulphuric acid to a mixture of sodium chloride and manganese ore (which is essentially manganese peroxide) and heating.

The commercial processes of preparing chlorine to-day are described in the following account in detail, in the order of their development:—

(a) The action of an aqueous solution of hydrochloric acid on one or other of the higher oxides of manganese, or their compounds at temperatures below 100°:

$$4HCl (solution) + MnO_2 = Cl_2 + MnCl_2 + 2H_2O$$
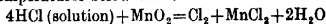
(b) The action of hydrochloric acid gas on atmospheric oxygen in the presence of catalysts (as copper compounds) at temperatures just below a red heat: $4HCl + O_2 = 2Cl_2 + 2H_2O$.

(c) The electrolysis of metallic chloride (as sodium chloride, potassium chloride, zinc chloride), which are occasionally anhydrous and fused, but are much more generally employed in aqueous solution. $2NaCl = Cl_2 + 2Na$; and $ZnCl_2 = Cl_2 + Zn$; the energy absorbed in these reactions is supplied electrically.

A number of proposals or non-important methods are briefly enumerated.

(a) The Aqueous Hydrochloric Acid and Manganese Oxide Method.—The solution of hydrochloric acid used is obtained in the manufacture of sodium sulphate that is salt cake; it is known as 'Commercial Hydrochloric Acid,' or as 'Muriatic Acid.' The solution used should be as strong as possible, because complete exhaustion of the acid by manganese peroxide is impracticable, and a residual liquor containing a considerable amount of unavailable acid is always left. The stronger the hydrochloric acid solution to start with the smaller the percentage of the total HCl which is lost (for actual figures, see below)

The manganese ore used for the generation of chlorine should contain a high percentage of MnO_2. The two next lower oxides of manganese also liberate chlorine, but only a smaller proportion of the total chlorine employed as shown by the following equations:—

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O$$
$$Mn_2O_3 + 6HCl = Cl_2 + 2MnCl_2 + 3H_2O$$
$$Mn_3O_4 + 8HCl = Cl_2 + 3MnCl_2 + 4H_2O$$
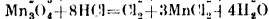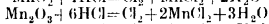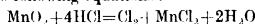
Pyrolusite is the manganese ore generally used; it usually occurs in distinctly crystalline masses of a fibrous structure; its sp.gr. is 4·7–5, and its colour iron-black to dark steel-grey with a metallic lustre; it also occurs as amorphous friable masses that soil the fingers. It has been mined in North Wales, and occurs in quantity in Germany, Bohemia, Transylvania, Russia, India, Australia, Japan, and the United States of America.

The chief source of the industrial pyrolusite used in this country is Southern Russia. The ore varies usually from 75 p.c. to 85 p.c. MnO_2. An average analysis of the Russian ore is: 80 p.c. MnO_2; 1 p.c. MnO; 3 p.c. H_2O.

It is customary to buy and sell manganese ore on the percentage of MnO_2 only.

The higher the percentage of MnO_2, the more valuable the ore, as the impurities, even if substances such as $BaSO_4$ and SiO_2, do harm by coating the particles of MnO_2 and preventing the action of the HCl, and also by adding to the amount of waste material to be handled. If the impurities are carbonates ($CaCO_3$, $BaCO_3$, &c.), they not only waste hydrochloric acid, but the CO_2 evolved during their solution harms the bleaching powder into which the bulk of industrial chlorine is made.

The physical condition of the manganese ore is also important, the softer ores being preferable

to the harder ones, which are more slowly acted on by the hydrochloric acid.

For generating somewhat small quantities of chlorine the generating vessel, or still, may be made of stoneware. Fig. 1 shows one of the best-known forms of stoneware stills, intended for heating from the outside in a water- or steam-bath, made of wood or masonry. The manganese is placed in the perforated cylinder, which holds about 1 cwt., and is put in and out by means of specially shaped tongs, through the large opening. The small necks serve for introducing the acid and taking away the gas At the end of the operation the still liquor is drawn off by a siphon, or by a discharge pipe passing through the steam-jacket Such small stills permit of careful and economical working so far as materials are concerned, since the acid is not diluted by condensed steam.
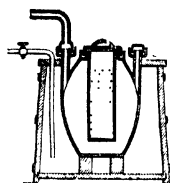
FIG. 1.

Fig. 2 shows a contrivance which allows the chlorine pipes and the main pipe to be instantly connected or disconnected. There is a Y-shaped lead pipe a, the upper arms of which are converted into hydraulic lutes by 'burning' an outer pipe, bb, on to them. The ends of the gas pipes, both that leading from the stills c, and that leading to the gas main d, are widened out into cups dipping into the water which fills the annular space at b. The rubber pipe e and its attached cup contain sufficient water to fill and thus stop the gas-way a whenever the pipe and cup are raised.
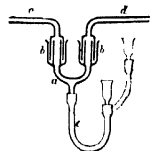
FIG 2.

For generating large quantities of chlorine the stills are made of silicious sandstone or other stone not acted upon by acids, not pervious to them, and not liable to crack by rapid changes of temperature. Such stone is found at Southowram, and is known as 'Yorkshire flag.'

A small old-fashioned stone still is shown in Fig. 3, which represents it cut through in the middle. The bottom is formed by a stone, 10 to 12 inches thick, with grooves for the sides to fit in. The sides are stone slabs, 5 to 6, or even 8 inches thick, and joined at the corners on the 'feather and groove' principle. The end stones project both ways over the sides, which fit into grooves cut in the end stones. The joints are made tight by dressing a small groove into the two adjoining faces, and placing a ⅝-inch india-rubber cord in the channel thus formed. The lid consists of one or more stones laid in a rebate, and the joint is made gas-tight by partly filling the rebate with a putty of linseed oil and china-clay. The diagram shows how the still is fitted with the following parts. A false bottom a; a pipe b, for the introduction of hydrochloric acid, sealed at the bottom by the acid in a small earthenware bowl; a leaden steam pipe, c, connected at the bottom with a stone or stoneware steam column

d, which is provided with side holes (not shown in the figure) situated a short distance above the bottom slab, for the issue of the steam into the acid, and at the top by the loop e with a tap f (the loop protecting the tap to some extent against the action of the chlorine); the earthenware or leaden gas pipe g, the connection of which with the gas main h can be opened or
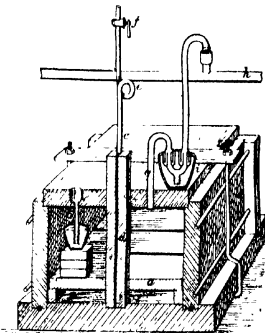
FIG. 3.

shut off at will by putting more or less water into the pot i. The man hole for charging the still and the discharging hole must be assumed to be provided in that half of the still not shown in the diagram These stills are made $7 \times 5 \times 3$ feet, inside measurement, and upwards.

Fig. 4 shows a still of the bevel-joint type, seen from above, with the cover removed; a are the flags forming the false bottom, one of which, a', is made to stand up; c is the steam stone, but the long central hole and the radial short holes for the passage of the steam are not shown; A, B, C, D are the rods binding the stones together by means of the cast-iron corner
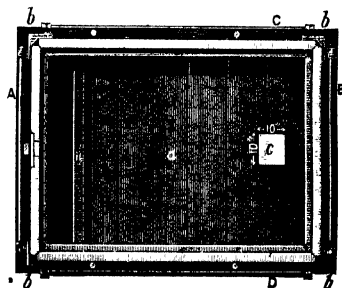
FIG. 4.

pieces b, b. The joints are made by the compression of the stones on to round rubber cords shown as black dots in each corner joint in the figure. The cord for the bottom joint may be one inch diameter, that for the upright joints may be ¾ inch diameter; the junctions of the several cords with each other are made liquor-tight by boring with a cork borer a comparatively

small hole in one cord, and then inserting the end of the other cord into the broad end of a hollow conical steel needle, which is smeared with glycerin, the second cord may be passed through the hole in the first cord and the small projecting end neatly cut off.

The Process.—In order to work the stills, those of smaller sizes, Fig. 1, where the manganese is contained in a sieve, are usually first charged with the requisite quantity of acid. The sieve containing the manganese (about 1 cwt.) is then put in, the cover is at once put on and made tight by water-luting or cementing, and the evolution of chlorine begins forthwith. When it slackens, heat is gradually supplied by turning on the steam till the acid is exhausted. The stills are then allowed to cool down, usually till the next morning. They are then opened, the sieve is lifted out, the manganese remaining in it is washed and replenished by more ore, the liquor is siphoned or run out of the still, fresh acid is run in, and a new start can be made at once.

The large stone stills are charged with from 6 to 10 cwts of manganese broken up into pieces, which must be smaller in the case of hard ores, but should not be too small, lest too much is washed down below the false bottom. The manhole is then closed and acid is run in, at first quickly, afterwards gradually, so that it takes several hours to run in the full charge All this time chlorine is given off, much heat being generated in the process, of course much more with concentrated than with somewhat dilute acid. When the evolution of gas becomes slow, steam is injected into the still, but very cautiously, as otherwise the water might be thrown out of the lutes, and only at intervals, for instance for 10 minutes every hour. Too much steaming causes too rapid an evolution of chlorine, and the volatilisation of much acid and water. The temperature of the stills ought never to get above 90°. It is preferable not to steam all the stills of a set at the same time, but in regular rotation, to produce a more continuous current of chlorine. Chlorine stills ought to be kept going at least 24 hours, but large stills are better kept going for 48 hours, as more of the acid will then be utilised.

When the waste liquid, ' still liquor,' is run off it emits an intolerable stench of chlorine, so that this operation is most irksome, both for the workmen and those people who live near the works. The 'still liquor,' even after being freed from its muddy constituents by settling, is, on account of its acidity, one of the worst nuisances for any watercourse into which it may be run. These nuisances have been completely overcome by the introduction of the Weldon process, where the still liquor from the fresh manganese ore is run into the Weldon stills, as described a little later on, and at works where chlorine is made on too small a scale to permit of applying the Weldon process, the still liquor now has to be run into a closed tank, and neutralised by chalk or limestone dust before running it away, even in a very diluted form.

The chlorine evolved in the stills is always contaminated with hydrochloric acid gas, and a considerable amount of aqueous vapour on account of its high temperature. To remove these impurities the gas is passed through a long string of earthenware or lead pipes, externally cooled by air (or, if needful, by water), so that the water vapour condenses, and the water produced dissolves the hydrochloric acid gas, and both are then drained away by trapped escape pipes.

The Chemistry of the Process.—The first reaction taking place in the chlorine stills is :
$MnO_2 + 4HCl = MnCl_4 + 2H_2O$ or (more probably)
$2MnO_2 + 8HCl = Mn_2Cl_6 + 4H_2O + Cl_2$.   (There is some discrepancy of opinion as to which of these two chlorides of manganese is formed. Compare W. W. Fischer, Chem. News, 37, 250 ; U. S. Pickering, *ibid.* 39, 225 ; Berthelot, Compt. rend. 91, 251.)

These chlorides, $MnCl_4$ and Mn_2Cl_6, form a dark-brown solution which quickly decomposes even at the ordinary temperature into $MnCl_2$ and free chlorine, so that the ultimate result is : $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$;   but this reaction is only completed at about 100° and with a certain excess of hydrochloric acid. Theoretically for 100 parts by weight of MnO_2, or an equivalent quantity of manganese ore, almost exactly 170 dry HCl or 530 acid of 32° Tw., ought to be consumed ; practically, at least, 10 p.c more is used, and with low-strength acid, hard manganese, direct steaming, &c., twice the theoretical quantity of acid may be required to be present.

The still liquor contains chiefly manganous chloride, free hydrochloric acid, the chlorides of other metals present in the ore, and a little chlorine.

Black's analysis of still liquor, in a well-conducted works, showed how incompletely the acid is utilised :

$MnCl_2$	.	.	.	.	10·6
HCl	.	.	.	.	6·6
Al_2Cl_6	.	.	.	.	0·6
Fe_2Cl_6	.	.	.	.	0·5
Cl_2	.	.	.	not determined	
H_2O (by diff)	.	.	.	81·7

100·0

On the assumptions that all the manganese in the ore was in the form of MnO_2, and that no hydrochloric acid gas was carried away by the chlorine, it follows that out of every 100 parts of HCl added 33·6 parts had been left untouched.

The free acid is tested for in daily practice by an easy but approximate method, namely to a measured volume of still liquor, standardised caustic soda liquor is run in from a burette till the formation of flakes of $Fe_2(OH)_6$, which do not dissolve on shaking, indicates the saturation of the free acid.

TREATMENT OF STILL LIQUOR FOR RECOVERY OF THE MANGANESE AND THE METHOD OF USING THE RECOVERED MANGANESE.   Many suggestions have been made and tried with this object, but one process has proved superior to all others, and is now universally adopted The first foundations of this process were laid in 1837, when Gossage precipitated the still liquor with lime, ran off the supernatant liquor, and agitated the precipitate with air ; the oxidation was, however, very slow, and was never so much as half complete.   In 1866 Walter Weldon made his first attempts, and

by 1869 his new process was in commercial use at Messrs. Gamble & Co.'s works at St. Helens, and by 1871–1873 had been so improved as to be adopted by all English and continental alkali works. The apparatus employed has received but few modifications, but the conduction of process, which in the critical part is complicated, and still not thoroughly explained, has been more modified. In the following the apparatus and process are described together, and in the sequence of events occurring when starting up a new plant.

Fig. 5 shows the plant in elevation.

The process is commenced in the stone still E, which has been already described in construction and process by Figs. 3 and 4 and the accompanying text. The only changes demanded by the Weldon process are : (1) That the acid employed should be as free as possible from sulphuric acid, because when subsequently the liquor is treated with calcium carbonate the voluminous crystalline needles of $CaSO_4\,2H_2O$ that are formed entail extra labour and expense in filter pressing and removing the filter cakes, and there is an accompanying loss of manganese chloride solution. (2) That the run-off pipe for the still liquor, instead of leading into a neutralising well, leads into a mud still D, which is shown in section in Fig. 5. The utility of this last change does not arise until a later stage in the process, and the special construction of this large mud still D will therefore not be now described

The still liquor may be at once run from D into one or other of the two neutralising wells G, G by means of pipes or covered channels not shown in the figure, and charge after charge of native manganese ore is dissolved in E in the same way, filling the wells G,G alternately and repeatedly for the next operation.

The neutralising wells G, G are sunk in the ground on a bed of puddled clay, and after being built are surrounded by puddled clay to prevent possibility of leakage : they are built of large stone slabs of acid-proof Yorkshire flag, as already described for the still E, except that it is much larger and is octagonal in shape ; their dimensions are, depth 6 feet, diameter 15 feet. On the top of the wells two large timber beams are seen supporting the agitators composed of wooden gates driven by short vertical shafts (situated above the liquor level), and large crown wheels and pinions situated above the timber beams ; the pinions are driven by one horizontal shaft and the small steam engine situated between the two left-hand mud stills D, D. The liquor, while continuously agitated, is slowly treated with crushed chalk or powdered limestone, which is preferably very finely ground. The free HCl is first acted upon, yielding calcium chloride, which is an essential component for the remaining processes, and carbonic acid gas, which in escaping carries away the small quantity of dissolved chlorine gas ; these two objectionable gases are prevented from escaping freely into the air by covering the wells with strong planks well tarred and by connecting them to the suction of the nearest chimney by an earthenware pipe. Towards the end of the operation the additions are made slowly, and with frequent testing of samples, by seeing if they effervesce when

poured on to ground chalk. When the free acid has been neutralised the ferric chloride, and aluminium chlorides shown in the preceding analysis are also converted into calcium chloride and ferric and aluminium hydroxides, and these last carry down as ferric arsenate any arsenious acid originally present in the muriatic acid. During this treatment any sulphuric acid present in the muriatic acid is converted, as already mentioned, into $CaSO_4.2H_2O$. Complete neutralisation is necessary to remove all the impurities named, and also to prevent corrosion of the settling tanks A, A, into which the liquor is next pumped, but the excess of $CaCO_3$ employed should be the smallest possible to reduce the cost of the subsequent settling and filtering operations and their loss of manganese liquor.

As soon as the neutralised liquor in one of the wells G is ready a swivel pipe is lowered from above into the liquid, as shown in Fig. 5, in the left-hand well, and the turbid liquor is then piped to the force pump shown in the figure in front of the third tank D from the left. The internal working parts of this pump are made of gun metal The figure shows the delivery pipe rising to the top of the plant, then running horizontally and discharging through control cocks into one or other of the four chloride of manganese settlers A, A, A, A. As soon as the well G is emptied and the pump stopped, a small valve is opened at the base of the pump delivery pipe, and the pipes thus drained back into the well ; the swivel pipe taking the liquor from the well is also withdrawn ; these things are done to prevent corrosion of the pipes. The well is then ready to receive its next charge, and so on.

The chloride of manganese settlers are made of ⅜-inch thick boiler plates, and are 18 feet by 12 feet and 6 feet deep, and therefore are carried by a very strong timber framework that rests upon the strong brick walls that carry the settlers C, C, C. As the stock of liquor in A does not fill the tank, and is moreover not sufficient for the next operation, the processes already described must be repeated until at least one settling tank A is quite full. After making the last addition a few hours' settling should allow the liquid to settle quite clear ; it is important that the liquor going forward to the next operation should be quite clear, otherwise the charge in the next operation is apt to froth over, and also the recovered manganese will consume an undue amount of acid.

As the correct proportioning of the manganese chloride liquor and the milk of lime in the following process are admittedly the key to the rapidity of the subsequent absorption of oxygen, and as no practical method of regulating this proportion is described in Lunge's standard work, " Sulphuric Acid and Alkali," and as it is admitted that milk of lime differs very considerably in its initial action on manganese chloride liquor, according to the source of the lime and the manner of making it into milk, the usual description is here slightly modified so as to contain a means of ascertaining and controlling the proportions of $MnCl_2$ and CaO used.

Having correctly measured the length and width of the settler A and the position of the
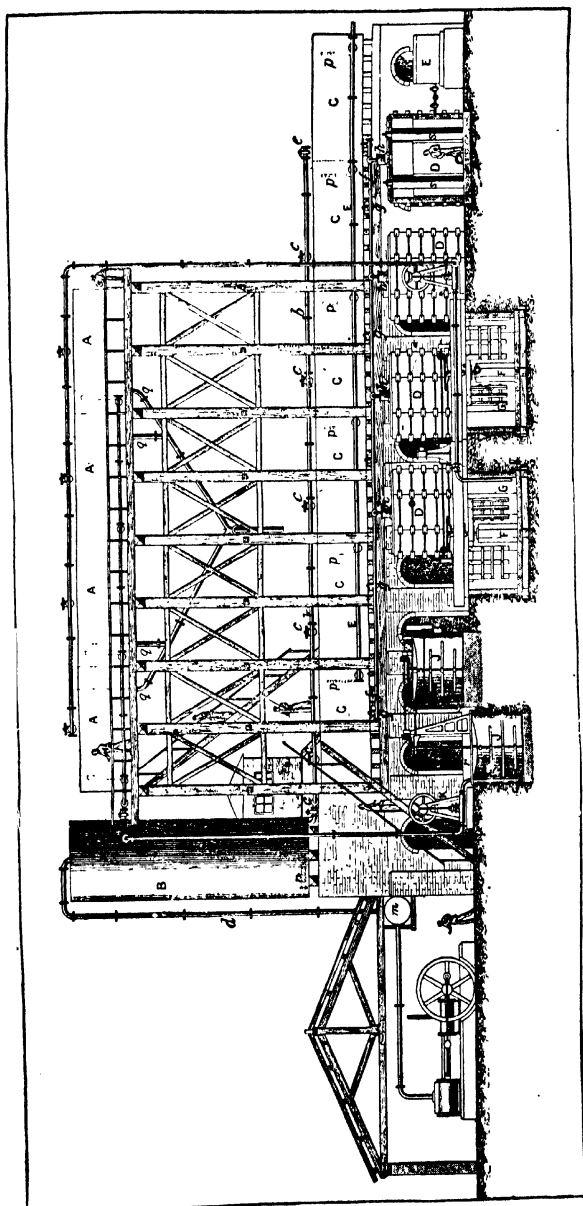
Fig. 5.

surface of the liquor, and recorded these measurements, and having also taken a sample of the liquor for analysis as shortly described, the clear liquor may be drawn off from the settler by lowering a swivel pipe just under the surface of the liquor, where the open end of the pipe can be inspected and the liquor above it can be seen to be quite clear. The bottom end of the swivel pipe is attached to the side of the tank about a foot above the bottom of the tank, so as to leave plenty of room for the mud to collect and to be stored pending its removal. Outside the tank the flow of the clear liquor is controlled by a cock, and cocks control its entrance into the oxidising tower B, shown in Fig. 5, or into a second similar tower situate just behind it. The treatment of the mud left in the tank will be described later, as it is first allowed to accumulate.

The oxidising towers B are made of ⅜-inch thick boiler plates, and they may be 8 feet diameter and 28 feet high, the bottom is flat, and the top is quite open. The pipe bringing the manganese chloride liquor enters the tower about 6 feet from the top of the tower, and as the tower shakes considerably during the subsequent operations, the connection between the tower and the clear liquor main is made through a short piece of indiarubber pipe. The diameter and height of the tower being carefully measured, its capacity when half full is calculated, and a further reckoning gives the new position the surface of the liquid will occupy in the settler A when the tower has been half filled, and as the liquor approaches this level the top of the swivel pipe may be set to give exactly the desired amount of liquor. When the liquor ceases to run the cocks are closed, and the residual liquor in the settler is reserved for the finishing of the charge as explained later.

The manganese chloride liquor should be tested for $MnCl_2$ by diluting a measured sample with boiling water, adding zinc oxide until the mixture is white as milk, and, lastly, adding standard potassium permanganate with occasional boilings, until the supernatant clear liquor shows a pink flush; the reaction yields a manganite exactly like the Weldon process under consideration $ZnO+MnO+O=ZnO\cdot MnO_2$, and the necessary oxygen is obtained from the permanganate similarly

$$3ZnO+2KMnO_4$$
$$=K_2O\cdot ZnO+2(ZnO\cdot MnO_2)+3O$$
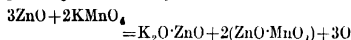
The percentage of manganese chloride having been calculated from the analysis, the lbs. of manganese chloride in the batch is then easily reckoned.

The temperature of the manganese liquor in the tower will be above atmospheric temperature, and in subsequent operations will be still more so, but experience has shown that if it is below 55° C., it should be heated to this point by blowing in steam. The steam pipe is not shown in the figure, and because of the shaking of the tower it must pass over the top of the tower, and terminates at the bottom of the tower in several branches containing perforations. The temperature is ascertained by drawing a sample from a sampling cock situated in the testing cabin, shown in the figure, from which

cabin there is easy access to all other parts of the plant.

The manganese chloride liquor during the above heating may be agitated, and for the subsequent operation must be well agitated. This agitation is effected by a blast of air. The blowing engine-house is shown on the left hand of Fig. 5. The right-hand cylinder and fly-wheel constitute the steam engine, the steam supply pipe being shown descending to the centre of the cylinder. The left-hand cylinder is the blower; the air is taken in on the ends of the cylinder through numerous valves of the flap type, faced with rubber, and is delivered through the pipe shown leading to the air pressure regulating vessel m, and thence by the 7-inch diameter pipe d over the top of the tower B, because of the considerable shaking of the tower during the subsequent operations, and thence to the bottom of the tower, where it ends in a cross or a gridiron of pipes, marked n in Fig. 5, that contain a multiplicity of perforations on their underside, so that the pipes keep themselves clear from the liquor and mud treated in the tower. When used for agitating purposes alone the blast of air required is not great, but the blast can be regulated as desired, and as described later, can be increased very considerably.

Milk of lime is required for the next operation, and it is prepared in the upper of the two tanks, J, J, shown in Fig. 5. Each of these tanks is made of boiler plate, and is provided with an agitator, the drive being effected by a small steam engine affixed to the right-hand side of the upper tank J, and transmitted by a shaft and two small bevel pinion wheels to either or both of the bevel crown wheels seen on the tops of the two agitator shafts. The upper tank only contains a lime cage, the bottom of which is indicated by a horizontal line above the third agitator blade; the cage is built of iron rods or perforated metal plates on the bottom and sides, the top of the cage is quite open. The tank is filled with water while steam is being also blown in, until the hot water stands well above the level of the bottom of the cage. Quicklime is selected so as to contain less than 1 p.c. of magnesia; it should be well burnt, but not over-burnt. The magnesia is very objectionable, because it accumulates during the repetition of the following processes, and in the generation of the chlorine it neutralises acid to no purpose; the method of removing it is described later. Well-burnt lime does not contain more than 2 p.c. carbonic acid, and it slakes quickly and completely, giving a milk that is particularly free from grit. Over-burnt lime slakes exceedingly slowly, and the resultant milk contains large quantities of minute grains of unslaked lime, that react only exceedingly slowly with water or the manganese calcium chloride liquor, and so remain inert until the chlorine is generated, when they neutralise acid to no purpose. The selected quicklime in the form of large lumps is put into the cage, it soon slakes, generating thereby much heat, and this addition is continued until the milk registers 50° on Twaddell's hydrometer, the test jar being gently rotated the while; the milk then contains 20 lbs. CaO per cubic foot, and is as strong as can be conveniently

either native or recovered MnO_2. Some processes patented after theirs (Henderson, 1871; Weldon, 1871; Wigg, 1873, &c.) proceed on the same lines, but have not been practically successful.

The Deacon process starts from the well-known fact that a mixture of hydrochloric acid gas and oxygen at a temperature just below a red heat, especially in contact with porous substances, partially changes into chlorine and water: $2HCl + O = H_2O + Cl_2$. This decomposition is very much assisted by the employment of substances which serve as oxygen-carriers, and of these the salts of copper (previously employed by Vogel, 1855; Gatty and Laurent, 1860, Mallet, 1866), have been found most useful. Probably in all cases cupric chloride is formed, which at once splits up into cuprous chloride and free chlorine. The Cu_2Cl_2 combines with oxygen to form oxychloride $CuO·CuCl_2$, and this acts again upon HCl, yielding water and reforming cupric chloride, so that the reactions can begin over again:—

(1) $2CuCl_2 = Cu_2Cl_2 + Cl_2$
(2) $Cu_2Cl_2 + O = Cl—Cu—O—Cu—Cl$
(3) $Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2$
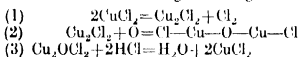
Theoretically, *all* the HCl would thus be converted into chlorine, but in practice, under the best conditions, about two-thirds of this decomposition is effected. The undecomposed HCl is, however, not lost, but is recovered and can be utilised for other purposes, *e.g.* for the Weldon process.

From a diagram constructed by Hurter, showing the affinity of technically available elements for oxygen, chlorine, and hydrogen, it appears that no other metal than copper forms two oxides and two chlorides, in which the combination is of so loose a character. It is therefore almost a certainty that a cheaper and equally efficient catalyst cannot be found, and that the Deacon process is the best for the direct conversion of gaseous HCl into free chlorine.

Deacon's process deals with the gaseous hydrochloric acid, as it is evolved in decomposing common salt by sulphuric acid without condensing it into liquid acid. This is evidently a great advantage in one way, but when the salt cake is made in the ordinary hand-worked pot and furnace, it has the drawback that in the beginning of each operation much more HCl, and hence more Cl, is got than afterwards. In practice, only the gases from the decomposing pots, say 68–70 p.c. of the total HCl, are used for the Deacon process, those coming from the roasters being too dilute and containing too much sulphuric acid. In order to equalise the operation to a certain extent, the gases from two salt-cake pots can be mixed and the pots worked alternately, so that the strong gas from the early part of one charge is mixed with the weak gas from the latter part of the other charge.

The quantity of air necessary to form chlorine enters through the joints of the doors and dampers. It is regulated by the speed of the aspirator (a Root's blower) or cast-iron fan, which is placed at the end of the whole apparatus and produces the movement of the gases through it. Usually there are 4 vols. of air to 1 vol. of

HCl. An excess of air is less injurious than a deficiency of it, in which case there is a poor decomposition.

The gases leaving the pot are first cooled by a long string of pipes and a scrubber; thus much of the water and about $\frac{1}{3}$ or $\frac{1}{4}$ of the HCl is removed. A patent by Deacon and Hurter (Eng. Pat. 2104, 1888) provides for cooling the gas and drying it in a sulphuric-acid tower before it enters the decomposer, such complete drying being very advantageous for the process. The gases now enter the heating apparatus. This is a furnace, 16 feet × 16 feet, in which twenty-six vertical pipes, 12 inches wide and 9 feet high, are arranged in two sets of twelve each, connected like the ' breeches pipes ' in the blast-heating stoves, formerly used in ironworks and now replaced by brick heaters.

The gases are here heated up to 500°; the waste heat of the furnace is sufficient for heating the decomposer, which does not possess any fire of its own.

The gases now pass into the decomposer (Fig. 6.) This is an upright cast-iron cylinder, 12 to 15 feet wide. It contains a cylindrical ring of broken bricks D, D, supported by two cylindrical cast-iron rings of shutters placed concentrically one within the other. The gases enter at the circumference
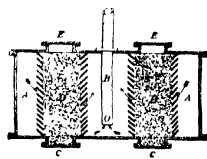
FIG. 6.

at A, pass radially across the decomposing mass D into the inner space, and are led away through the pipe OB. The annular space between the shutters is 3 feet wide, and is divided into six compartments, one of which is emptied every fortnight. This is done by means of the discharging doors C, C below the cylinders. Fresh decomposing material is then thrown in from above through E, E; this material consists of burnt clay broken up into lumps, or ordinary bricks broken, freed from dust, and dipped into a solution of cupric chloride. The mass contains about 0.6–0.7 p.c. of metallic copper. After the active substance has served once, that is, for 10 to 12 weeks, it is thrown away. Each cwt. of clay produces about 10 to 12 cwts. of bleach. It has been found useless to attempt utilising the contact substance by redipping it in the copper solution or in any other way. The cost of copper for the contact substance does not exceed 1s. per ton of bleach produced.

The temperature, both in the heating apparatus and in the decomposer, must be most carefully regulated, for which purpose special pyrometers have been constructed (*cf.* Hurter on Pyrometers, J. Soc. Chem. Ind. 1886, 625). In the decomposer, it ought to range from 480° to 500°.

When the gases leave the decomposer, they consist of a mixture of HCl, free Cl_2, and steam. In the best case, two-thirds of the HCl is converted into chlorine, but sometimes only one half. The hot exit gases are now cooled by passing through a long string of earthenware or glass pipes, and are then freed from HCl by washing with water in the ordinary acid condensers,

consisting of stone towers filled with coke, combined or not combined with acid cisterns, Woulff's jars, &c. By properly managing this process, all the acid can be obtained in the strong state, as required for the Weldon process and other purposes.

The gases can now be employed directly for making bleach liquor or chlorate liquor from milk of lime. If, however, bleaching powder is to be made, they must be freed from water because the ratio of water to chlorine is so great that strong bleaching powder could not be made; the amount of water depends on the temperature, and can be found from tables of the tension of aqueous vapour; the amount of chlorine is at most 10 p.c. by volume. The water is removed by passing the gases through a lead tower packed with coke, down which sulphuric acid of not less than 140° Tw. is kept flowing.

As will be seen from the description, there is theoretically no loss of HCl in the Deacon process, the whole of the acid evolved from the salt being either converted into chlorine or recovered by condensation as liquid hydrochloric acid. In practice, of course, some losses occur, but they are not necessarily large, and their amount depends principally on the efficiency of the draughting arrangements and the avoidance of low-level escapes at the salt-cake pots and furnaces. The fuel used per ton of bleaching powder to heat the decomposing apparatus depends naturally on the efficiency of working of the process, and varies from 6 to 10 cwts. per ton of bleaching powder

During the early years of its existence, the Deacon process had many difficulties to contend with, and the working results were disappointing and unsatisfactory.

The fact that the impurities accompanying the gaseous HCl were sufficient to seriously affect the process was not realised. The impurities are sulphuric and sulphurous acid, arsenious acid, water, and carbon dioxide.

The sulphuric acid and sulphurous acid carried along with the gaseous HCl, especially when attempts were made as they frequently were in the early days, to utilise the roaster or furnace gas as well as the pot gas, converted the $CuCl_2$ into $CuSO_4$, which requires a higher temperature and gives a lower decomposition than $CuCl_2$.

The arsenious acid derived from the As_4O_6 in the sulphuric acid used forms arsenate of copper, which is even less reactive than the $CuSO_4$. The presence of these impurities necessitated the frequent renewal of the decomposing material. Water is one of the products of the decomposition, and hence, when present in the inlet gases, increases the partial pressure of the products of the reaction and lowers the maximum p.c. decomposition obtainable under the conditions of the process.

Carbonic acid derived from the fuel gases, either of the salt-cake furnaces or of the decomposing furnace itself, was a serious obstacle to, and frequently entirely prevented, the production of strong bleaching powder. This difficulty has been overcome by greater care in the construction of the apparatus and testing for leakage.

It will be noted from the above description

that only the gaseous HCl from the salt-cake pot is dealt with by the Deacon process, and that allowing for the liquid acid collected after the decomposers, about 60 p.c. of the total acid is obtained in the liquid form, and has to be sold as such or used in some other way such as by the Weldon process.

Hasenclever, however (Eng. Pat. 3393, 1883), describes a process for gasifying the HCl in the liquid acid by mixing with strong hot sulphuric acid in a series of earthenware vessels through which air is blown. By this means, a steady continuous stream of gaseous HCl is evolved with an easily regulated supply of air. After passing through the series of vessels, the vitriol diluted with the water contained in the liquid hydrochloric acid has to be reconcentrated to the original sp.gr. The concentration is generally performed in long, lead brick-lined pans, heated by top heat, the fuel gases being in direct contact with the sulphuric acid. This process is used to a considerable extent, but from the large quantity of sulphuric acid to be concentrated per ton of bleaching powder, a very material addition is made to the cost of manufacture.

Other contact substances—Many substances have been the objects of proposals, some of which are inseparable from the manufacture of chlorine from metallic chlorides, that is, from HCl in the nascent state. A general investigation on the mutual action of HCl and O in the presence of certain metallic compounds (of Cu, Fe, Mn, and Cr) was made by Lamy (Bull. Soc. chim. 1873, 20, 2). We must refer to the original, and will only mention that copper salts were found to be much more efficient than others, and that with these the decomposition is at its maximum at about 440°.

The proposals to employ ferric chloride (Thberge, 1855, and others) or chromic oxide (Hargreaves and Robinson, 1872) have not had any practical success.

Nickel oxide was proposed by L. Mond (Eng. Pat. 8308, 1886). He passes HCl over heated NiO, when the chlorine combines with the base. The product is then in the same apparatus exposed to dried and heated air, whereby NiO is reformed and Cl is given off. In order to increase the active surface, pumice stone is impregnated with the chloride, and after drying the mass is exposed to the action of the gases in cylinders made of earthenware or enamelled iron. The gaseous HCl and air being previously heated, the retorts do not require very much additional heat from without, and therefore can be made of a large diameter. It is claimed for this process that it converts the HCl completely into chlorine, and that impure HCl, which is unfit for the Deacon process, is here quite suitable.

De Wilde and Reychler proposed (Eng. Pat. 17272 and 17659, 1889) to employ a mixture of magnesium and manganese chlorides with magnesium sulphate. The reaction takes place in two stages.

(1) $Mn_3O_8Mg_3 + 16HCl$
$$= 3MgCl_2 + 3MnCl_2 + 8H_2O + 4Cl$$
(2) $3MgCl_2 + 3MnCl_2 + 8O = Mn_3O_8Mg_3 + 12Cl$
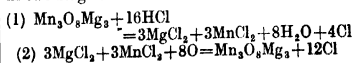
The process is not, as far as is known, actually worked.

(c) *The electrolysis of metallic chlorides method.*
—Recent years have seen a large development of electrolytic processes for the decomposition of metallic chlorides, chiefly those of sodium and potassium into chlorine and alkali. It was observed as early as 1800 by Cruikshank that on electrolysing a solution of common salt, caustic soda was formed at the negative pole. Berzelius, Hisinger, and Davy all worked on the same subject, but a long time elapsed before their observations were utilised in actual manufacture.

The difficulties experienced in the electrolytic decomposition of alkaline chlorides on a manufacturing scale have been first the cost of the electric current which was absolutely prohibitive until the dynamo-electrical machine had been so far developed as to be a commercial reality, viz. in 1872 by Gramme, and when it became possible to conduct electrolytic experiments on the large scale over long periods of time, it was soon found that there were many and serious difficulties as the corrosion of the anodes, the evolution of gas from the cathode, the diaphragms were either excessively porous or not sufficiently porous, and they disintegrated rapidly, there were excessive resistances, voltages, and the generation of heat, and there were secondary reactions, so that neither the chlorine nor the alkali metal product was obtained in the expected purity or quantity.

The various electrical processes suggested or tried for the decomposition of alkaline chlorides are all attempts to overcome economically these difficulties.

Theoretically a current of 1 ampere liberates in 1 hour 1·3236 grams of chlorine.

The number of patents taken out since the year 1885 in connection with electrolytic cells for the production of chlorine, is enormous, embodying every variety of shape, design, and method of work. We shall only deal with a few representative samples, illustrating the broad classes of design which have, up to the present, been used industrially on a large scale.

In describing these developments of the electrolytic processes, and their effects upon Leblanc's process, Lepsius in Berliner Berichte (1909, 2915) says, with German pride, that it is no wonder that the electrolytic process was first carried out in Germany, the richest country of the earth in salt and potash, and while he pities the fate of poor Leblanc, yet he concludes with characteristic German military imagination and arrogance, that the bitter international struggle between the old process born in France and developed in England, and its two younger rivals, is now finished after the crippling caused by the Belgian rival, The Solvay Ammonia Soda Process, because there appeared a German rival, the electrolysis of the alkali chlorides, whose victorious conquest of the chlorine market and other successes caused such annihilating wounds that the hundred-year old process was no longer able to stand.

Electrolysis of Potassium and Sodium Chlorides.

The cells may be roughly divided into four classes.

I. The cells in which the electrolyte consists of the fused salt.

II. The cells in which the electrolyte is a salt solution, and in which the cathode and anode are separated by a porous partition.

III. The cells in which the electrolyte is a salt solution, and in which a moving mercury cathode is used to receive and remove the sodium produced.

IV. The cells in which the electrolyte is a salt solution, and in which the caustic soda solution produced is only kept from mixing with the brine undergoing electrolysis by reason of the greater sp.gr. of the former.

Class I. *The Cell with the Fused Electrolyte.*—The best known examples of this cell are the Vautin and the Acker cell.

The Vautin cell (Eng. Pat. 13568 of 1893 and 9878 of 1894) electrolysed fused NaCl or KCl, with or without the addition of fluorides or other chlorides to lower the point of fusion, over a cathode of molten lead or tin with which the sodium or potassium formed an alloy. (*See* paper by Vautin, J. Soc. Chem. Ind. 1894, 448.)

The Acker cell is designed on the same principle as the Vautin cell and makes use of the lead cathode (*see* Eng. Pat. 6636 and 6637 of 1898). Below is a sketch (Fig. 7) of the Acker

SECTION a b SECTION c d
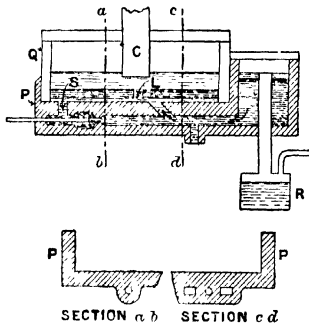
FIG. 7.

cell, taken from a paper by J. B. Kershaw in Electrician, Oct. 25, 1901. The bottom of the cell r is trough-shaped and of cast iron. It serves as electrical connection between the main conductor and the mass of fused lead L resting on it. The upper part of the cell Q is constructed of any refractory basic material not attacked by chlorine gas or fused salt. The anode c is of carbon and dips into the fused salt. The channels and subsidiary vessel R are arrangements designed to remove and decompose the lead alloy as it becomes sufficiently saturated with sodium. The decomposition of the alloy is effected by blowing steam into it, and the heat generated by the conversion of the sodium into hydroxide is returned to the cell and assists in maintaining the necessary temperature. The voltage actually taken by the Acker cell is 6·75, and the current efficiency 54 p.c. (Report of Commission on Science and Arts, J. Franklin Inst. 1903, 156). The Acker cell was worked at Niagara Falls on an industrial scale, from about 1900 to 1907, when the works were completely burned down and have not been rebuilt.

Class II. *The Porous Diaphragm Cells.*—The best known of the diaphragm cells is the Griesheim cell, which has been used on a very large scale in Germany, and also in Spain, France, and Russia.

Fig. 8 represents the cell in longitudinal sectional elevation, Fig. 9 represents it in plan,
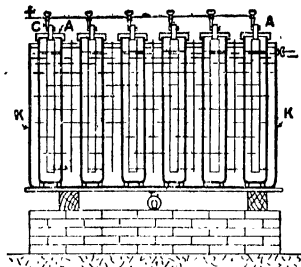
FIG. 8.

and Fig. 10 represents it in cross sectional elevation. The plate upon which the cell rests is shown by Figs. 8 and 10 to be insulated from
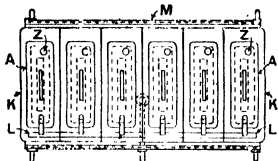
FIG. 9.

the ground by wooden bars, this is so that a number of such cells may be run electrically in series. The containing bath KK, Fig. 8, KMK,
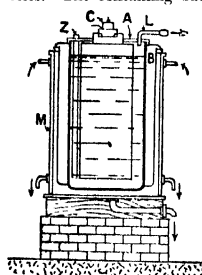
FIG. 10.

Fig. 9, M, Fig. 10, is built of sheet iron, and its two long sides are each covered with a steam jacket M, the object of which is to increase the temperature of the electrolytes and so to reduce their electrical resistance. The negative electrical lead is attached to the iron bath as indicated by the binding screw, lead and − sign on the right-hand side of Fig. 8. The bath is closed by a cover cut into segments and shaped so as to allow of the insertion of the five hanging iron cathode plates B, Fig. 10, and shown but not lettered in Figs. 8 and 10, and the six porous anode compartments A shown in each figure. Water is supplied to the tank K by a pipe (not shown), and by the electrolysis of the brine in the anode compartment is converted into a

caustic soda solution and hydrogen; the caustic soda solution is drawn off by the pipe under the centre of the tank shown in all the figures; the hydrogen gas is led away by a pipe not shown to gasholders for subsequent use. The anode compartments are composed of iron frames covered inside with cement, in the frames are set and cemented the porous diaphragms in large flat sheets. These porous diaphragms were made by mixing cement, common salt and hydrochloric acid in due proportions into a paste, and then forming into the shape required; when the salt subsequently dissolves the diaphragm becomes very porous. The anode compartments contain the anodes, which were first the ordinary pressed carbons, then gas retort carbons, and then carbons prepared in a special anode works, where the large pressed plates were roasted at the highest temperature of a porcelain kiln. These special anodes had a life of twelve months. The Figs. 8 and 10 show them passing through the covers of the anode compartments, and the external electrical connections C. Each cover also contains a long tubular earthenware basket Z, Figs. 9 and 10, for the addition of solid salt and a pipe L, Fig. 10, for the escape of the chlorine gas. The covers on the bath, and on the anode compartments, having been made gas tight by cement, all the anode connections are electrically connected as shown in Fig. 8, all the chlorine pipes are connected into a main LL, Fig. 9, and the electrical current may then be forced through the cell.

When the process has proceeded so far that the cathode liquor contains about 8 p.c. caustic potash or soda and about 14 p.c. of the corresponding chloride, it was found that the chlorine gas contained several per cent. of carbonic acid, and as this interferes with the use of the chlorine for making bleaching powder, and as the destruction of the anodes is too costly, the process is interrupted by stopping the current and running off the cathode liquor; the cathode compartment is then refilled with fresh brine and the current restarted. The cathode liquor is then evaporated in large double or triple effect vacuum evaporators until it contains 50 p.c. caustic alkali, during which all but a small quantity of the accompanying chloride crystallises out and is afterwards returned into the process.

The corrosion of carbon anodes led to their replacement by cast anodes of magnetic oxide of iron prepared by fusing ferric oxide in the electric arc furnace, whereby there is also a partial reduction. The anodes are difficult to prepare, but they have a good conductivity, and they last indefinitely. With oxide of iron anodes there is no further trouble from carbonic acid, but the anode liquor then contains potassium chlorate which crystallises out and is removed periodically and utilised. This output of chlorate can be increased at will by increasing the strength of the caustic alkali in the cathode compartment.

These magnetic anodes were exported by Germany to America, but when war was declared the supply was stopped and a number of attempts were made to produce them in America. Their great drawback is their extreme brittleness, but it has been found that this can be reduced to

one-half by suitable slow cooling or annealing, and that it can also be reduced to one-third by the admixture of about 5 p.c. of copper oxide, and by combining both modifications rods of 3·9 cm. when supported at 17·8 cm. apart require a weight of 119 kg. in the middle before they snap (Thompson and Atchison. Trans. American Electrochemical Soc. 1917, 213.)

These cells in Griesheim absorbed from 1884–1892 400 h p, after which it was increased to 800 h.p., and soon after to 2000 h p ; by 1894 installations began to be erected elsewhere, Bitterfeld in Saxony, Westeregeln, Ludwigshafen, Lamotte in France, Flix in Spain, and Slawjansk in South Russia, by 1909 the total h.p. absorbed by this cell was 33,000 (Lepsius. Ber. 1909, 2895.)

The Hargreaves-Bird Cell—The following illustration shows the Hargreaves-Bird cell (Eng Pat. 18871 of 1892 ; 5197 and 18173 of 1893). The peculiarity of this cell is that the diffusion of the cathode and the anode liquids into each other through the diaphragm, which takes place in ordinary diaphragm cells, is in this cell largely counterbalanced, as far as the diffusion of the cathode liquid is concerned, by employing a very considerable hydrostatic pressure on the anode liquid. This electrostatic pressure is, however, not sufficient to force any noteworthy amount of anode liquid into the cathode compartment because the diaphragm is in the ordinary sense nearly liquor tight, but it is yet sufficiently porous to allow the cation, sodium, with its electrical charge to pass through under the driving force of the electric current. The Fig. 11 is a vertical and diagrammatic cross

CENTRE CORE OF ANODE.
STONE COVER.
CATHODE CHAMBER.
CEMENT.
CATHODE CHAMBER.
ROUGH BLOCKS OF GAS CARBON.
ANODE CHAMBER.
ANODE CHAMBER.
DIAPHRAGM & CATHODE.
DIAPHRAGM & CATHODE.
RUN OFF PIPE.
RUN OFF PIPE.
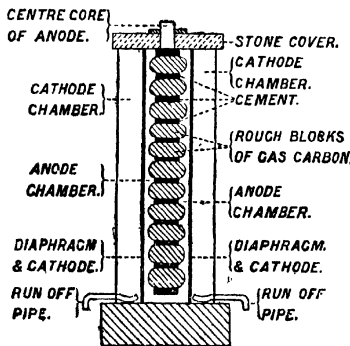
FIG. 11.

section of the cell. It shows two thick lines marked 'Diaphragm and Cathode'; each of these consists of a sheet of iron wire gauze on to one side only of which is plastered first a layer of asbestos pulp, and then a layer of Portland cement. The frame of the cell consists of a long base shown in the figure and two uprights not shown in the figure: turning the cement sides of the two "diaphragm and cathode" plates towards each other they are so firmly pressed against either side of the base and uprights as to form a watertight cell marked 'anode chamber,' at the same time electrical contact is made

between the iron wire gauzes and the negative electric conductor. Two other sheets of thin iron are then similarly pressed against corresponding ledges provided in the base and uprights, but not shown in the figure, so as to make with the two 'diaphragm and cathode' plates two chambers marked 'cathode chamber' in the Fig. Into the anode chamber is placed the anode built up of blocks of gas retort carbon on a central leaden core and also the brine to be electrolysed. Into the cathode chamber no liquor as such is put, but steam is blown in, which by heating the anode cell condenses as water on the cathode and so continually converts the sodium deposited by the electric current on the wire gauze cathodes and washes the solution of caustic soda formed down to the bottom of the cathode chamber, from whence it flows by the trapped run-off pipes As it was found that a higher efficiency was obtained by passing also carbonic acid gas (the exhaust from gas engines) into the cathode chamber, the manufacture of caustic soda was abandoned and replaced by the manufacture of sodium carbonate

A paper on this cell, by Hargreaves (J. Soc. Chem. Ind. 1895, p. 1011), states the current density as 18·7 amperes per square foot of diaphragm ; the voltage required for the preceding current as 3·4 volts; the current efficiency as 80·3 p c , and that the resultant soda liquor contains per 100 molecules Na_2CO_3, only 3·0 molecules NaCl if ordinary care is exercised, but that it is possible to reduce this amount to only 0·03 molecule. The present working is understood to give a current efficiency of about 90 p.c., and to require 4 volts per cell.

The Townsend Cell (Eng. Pat. 18403 of 1904) resembles the Hargreaves-Bird cell with this difference, that the cathode compartment is filled with kerosene oil which squeegees the alkali as it is formed off the cathode, and thus makes it possible to produce chlorine and caustic soda in this type of cell without great loss of current efficiency. Kershaw (Electrician, April 24, 1908) gives the current efficiency as 90 p.c., and the voltage per cell as 4·7. In the Seventh International Congress, 1909, 10, 36, Baekeland describes the result of 3½ years' work at Niagara with 1000 kilowatts ; the old cells were made for 2000 amperes, but new cells to consume four times this power will be capable of taking 6000 amperes. The current density per square foot of anode surface has also been increased from 100 amperes to 144 amperes. The attack on the carbon anodes requires the cleaning of the cell in about 30 days, which is a very simple matter, and the graphite anodes are so arranged that they can be repaired, and are ultimately entirely consumed. Aluminium conductors last longer than copper conductors in atmospheres where small amounts of chlorine are occasionally present. The hydrostatic pressure in the anode chamber is regulated so that with a cell using 2500 amperes, the amount of liquor passing through the diaphragm is most advantageously 24 litres per hour, which gives a soda liquor containing per litre 150 grm. NaOH and 200 grm. NaCl, and under these conditions the anode liquor contains but little hypochlorite and chlorate and consequently the chlorine has a satisfactory degree of purity.

The Finley Cell (Eng. Pat. 1716 of 1906) has a double diaphragm dividing the anode and cathode compartments. The diaphragm is very open in texture, and the brine feed for the cell is run into the centre compartment between the two diaphragms, from where it passes outwards on either side to the anode and cathode compartments. In this way, an additional obstacle, depending for its strength on the speed of feed of the brine, is interposed to prevent intermixture of the products of the electrolysis.

The diaphragms are made of asbestos 2–3 mm. thick, and the compartments are also only a few millimetres thick ; the diaphragms and frames are bolted together in any number after the fashion of a filter press. (Seventh International Congress of Applied Chemistry, 1909, x. 42)

Class III. *The cells in which the electrolyte is a salt solution, and in which a moving mercury cathode is used to receive and remove the sodium produced.*

The mercury cathode for the preparation of alkali metals was first used by Davy, it was described in an application for a patent (Eng Pat. 4349 of 1882) by Nolf It is mentioned again in Hermite's patent, 3957 of 1886. Further patents describing its use are Hermite and Dubosc, Eng. Pat. 21959 of 1891 ; Greenwood, Eng. Pat. 5999 of 1891.

The general principle of these cells is that the electrolysis takes place between an anode above and a cathode of mercury vertically below. The chlorine liberated naturally rises upwards and out of the solution, and the sodium or potassium freed combines with the mercury to form an amalgam. The amalgam, when sufficiently highly saturated with the alkaline metal, is replaced by fresh mercury and the amalgam itself decomposed by water, with the liberation of H₂ and the formation of a caustic alkaline solution.

The current efficiency of the modern mercury cell is stated to be not less than 90 p.c , and the voltage required 4 3 volts

Professor Lepsius (Ber. 1909, 2903) enumerates the following advantages and disadvantages of the mercury cell as compared with the diaphragm cell :—

The advantages of the mercury cell are : (1) the purity of both the chlorine and the caustic alkali produced, which are very important advantages ; (2) the comparatively high concentration of the caustic solution ; (3) the high current efficiency.

The disadvantages of the mercury cell are :— (1) the higher voltage, 4 3 volts as against 3·5 volts in the diaphragm cell ; (2) the cost of the mercury, of which 72 tons are required for a plant utilising 6000 h.p. ; (3) the greater cost of installation apart from the question of the mercury.

The various patents taken out and cells suggested differ chiefly in the method adopted for the movement of the mercury. To Castner, however, belongs the chief credit of making the mercury cell technically successful.

Castner's Rocking Cell.—Castner (Eng. Pat. No. 16046 of 1892) employs a moving mass of mercury, connecting up the anode and cathode chamber. Patent No. 10584 of 1893 makes the movement of the mercury by a rocking motion of the cell, see Fig. 12, which represents the original rocking cell. A is the cell divided into
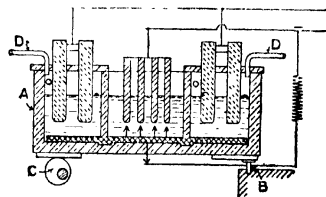
Fig. 12.

three compartments, and resting on the right-hand side on adjustable knife edges B. The left-hand side of the cell rests on an eccentric, C, revolving on a shaft ; this gives the rocking motion The two outer or anode compartments have carbon anodes and are filled with saturated brine ; the centre compartment contains iron cathodes and is filled with NaOH solution. A layer of mercury, about ¼ inch thick, lies on the bottom of the cell and alternately flows from first one and then the other anode compartment into and through the cathode compartment into the other anode compartment. The chlorine liberated in the anode compartment is carried away by pipes DD.

Castner, in the Chemical Trade Journal, 1894, 211, stated that the results of 1 week's work on a unit of 28 working cells, arranged in two parallel series of 14, gave a yield of 930 lbs. chlorine and 1120 lbs. NaOH per 24 hours ; the amperes used averaging 571, and the volts 55·1 or 3·9 per cell.

In 1895 the Castner Kellner Alkali Co. was formed to work this cell. Works were erected in Runcorn with 1000 h.p , and other similar works were soon erected abroad, viz. at Osternieuburg near Bernburg with 1500 h.p. by the Deutsche-Solvay Werke, at Augsburg by Meister Lucius & Bruning, at Jemappes near Brussels with 1000 h p , at Liubimow in Russia, at Jaice in Bosnia with 1300 h.p., and at Niagara Falls, N. America, by the Castner Electrolytic Alkali Co. in 1901 with 6000 h.p. (Lepsius, Ber 1909, 2903.)

Kellner Pressure-displacement Cell.—In this cell the chlorine compartment is placed in the
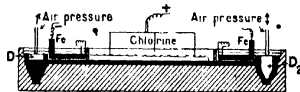
Fig. 13.

centre of the cell and on either side of it is a caustic compartment, each of which is provided on its further side with a recess, DD, which forms the alternative receptacle for the mercury. In these receptacles are immersed pressure vessels open at the bottom and connected at their tops to compressed air supplies which are automatically so regulated that the mercury is forced to move continuously from side to side by compressed air.

Above (Fig. 13) is a sketch which shows the construction and working of the cell, taken from the Chemiker Zeitung, Oct. 30, 1909.

The anodes are platinum gauze of which 1 gram is made to cover four square inches, and are placed in a cement box which has proved more satisfactory than the stoneware jars formerly used. Each cell contains six electrode boxes, and each box holds 88 pieces of platinum gauze. The cathodes are cast iron, cast in grill shape, and the primary battery, sodium amalgam—caustic solution—iron, acts independently of the main current through the chlorine cell, and also regulates itself. The current used is 4000 amperes per cell.

The great advantage of this cell is the high-current density which has resulted in considerable reduction of plant.

The Kellner-Solvay Scoop Wheel Cell.—This cell consists of two slanting troughs communi-
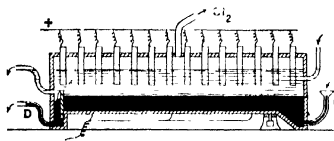
FIG. 14.

cating with one another at each end, in which the mercury is kept in constant circulation by a rotating scooped wheel placed between the two troughs at the one end. This cell is built in very large units, taking up to 10,000 amperes, and it is said that a 15,000-ampere cell is well within the bounds of possibility.

Fig. 14 is a diagrammatic sketch of the chlorine side of the cell, B being the mercury inlet and D the outlet for the amalgam; the scooped wheel is, however, not shown, neither is the caustic side of the cell.

Whiting Cell.—A cross sectional view of this cell is shown in Fig. 15. The right-hand side shows in the upper portion the cement cover with its attached graphite anodes and connections being lowered into the brine cell below, which consists of a number (say five) of separate compartments. From each of these in turn, and at intervals of two minutes, the mercury amalgam is entirely emptied by the automatic lifting of poppet valves, which are operated by the little shaft and cams shown above the cells towards the left; and the liquid amalgam runs over the graphite plates lining the three-fold zic-zac runway shown on the left of the figure; these plates and the amalgam being immersed in water act as a primary cell and generate caustic soda solution, hydrogen and pure mercury. The mercury next reaches the scoop wheel and by arrangements not shown in the figure is lifted and flows to the right side of the figure, whence it enters each cell in rotation. The ebb and flow of the mercury is used to admit fresh brine supplies to each compartment. This complicated arrangement is made to prevent the unequal flow of mercury and the formation of sodium amalgam of excessive strength. The cell was operated at the

Oxford Paper Co., Rumford, U.S.A., and is described in Trans. American Electrochem. Soc., 17, 327 (1910).

The new Castner-Kellner Cell differs essentially from the Kellner-Solvay cell only in the method of conveyance of the mercury, which, in this case, is effected by means of an Archimedian screw. Taussig, Zeit. für Elektrochemie, 1909, 659.

Class IV. The Specific Gravity Cell.—The best known cell of this type is the so-called 'Glocken Cell,' patented by the Oesterreichischer Verein für Chemische und Metallurgische Produkte, and from 1901 working on a large scale at Aussig in Bohemia, Berlin, and Stassfurt.

Fig. 16 is a diagrammatic sketch, in which A is the anode and K the cathode, separated by the non-conducting and impervious walls D, E of the bell G. The bath W is filled with salt solution, which enters at L and overflows at the pipe F. The chlorine escapes at C. These walls are required to keep the ascending current of hydrogen gas arising from K quite distinct and separate from the ascending current of chlorine gas arising from A. The anode and cathode are both situated in the upper parts of the electrolyte, and these parts are greatly agitated by the ascending gas bubbles—but the lower portions of the electrolyte are almost entirely stagnant and serve only as a means of conducting the electric current from the anode to the cathode. As the brine around the anode loses a portion of its chlorine by escape of the gas, and loses a corresponding portion of its sodium by electric migration of the cation Na' towards the cathode, this layer of liquid becomes continually lower in specific gravity and would ultimately lose all its dissolved salt were it
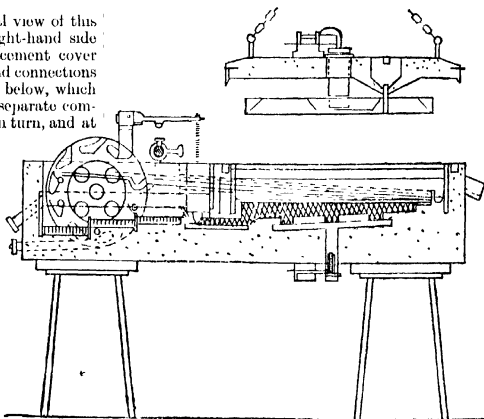
FIG. 15.

not for the constant feed of fresh brine at L; the quantity of this feed is such that it is only partly able to counterbalance the reduced gravity. On the other hand, the sodium liberated on the cathode forms with the adjacent brine an intensely strong film of caustic soda

solution, which falling by its high specific gravity into the lowest part of the cell forms a
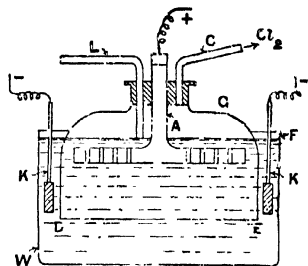
FIG. 16

heavy layer there which is scarcely disturbed by the slow current of weak brine from the inside of the bell trickling past the edges of the bell to be partially converted into caustic soda and hydrogen before it passes away by the exit pipe F
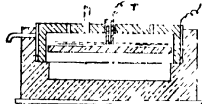
FIG. 17

Figs. 17, 18, and 19 are diagrams of the actual cells; Fig 17 being a cross sectional eleva tion, Fig 18 a plan, and Fig 19 on the left-hand side a longitudinal sectional elevation of the bell and its attachments, and on the right-hand side a cross sectional elevation of the same. The
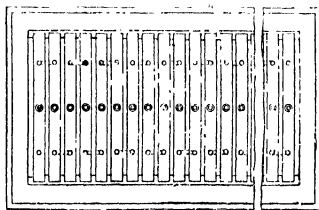
FIG. 18.

outer containing vessel is seen to contain two ledges to carry the bells, of which there are a great number in each cell. The junction of the anode with its conducting stem is badly shown
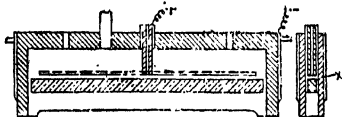
FIG. 19

in the figures. The brine supply is different from that shown in Fig. 16, for, to prevent the agitation of the electrolyte by the inflow of brine, the supply pipe is made to traverse the whole length of the anode, its two ends are closed and the brine escapes by a number of small holes along its upper side. The main portions of the cathode are best seen on the right-hand portion of Fig. 19 at x. The chlorine passes from bell to bell by the connecting arms shown in Fig. 18, and then makes its exit from some particular bell by the larger pipe shown in Figs. 17 and 19, but not shown in Fig. 18. The electrical con nections are indicated diagrammatically in Figs. 17 and 19 only. Each bell takes about 22 amperes at 4 volts. (Lepsius, Ber. 1909, 2904.)

Electrolysis of Zinc Chloride.—The waste calcium chloride from the ammonia soda process has been utilised since 1897 by Brunner Mond and Co., of Winnington, as a source of chlorine. By heating the liquor with crude zinc oxide and carbon dioxide the reaction $CaCl_2 + ZnO + CO_2 = ZnCl_2 + CaCO_3$ takes place, or by treating it with native zinc carbonate (calamine) the reaction $CaCl_2 + ZnCO_3 = ZnCl_2 + CaCO_3$. The filtered solution of zinc chloride is freed from its impurities (amongst which is a not inconsiderable amount of cadmium) and the resultant solution is electrolysed with carbon anodes and circular revolving cathodes that are only partially immersed, to produce chlorine gas and an exceedingly pure metallic zinc. Many of the details are due to C. Hopfner (Brit. Pat. 11724 of 1894, and D. R. P. 85812 of 1895). Fuller details are given in two volumes of Monographien uber angewandte Elektrochemie, namely—Die Darstellung des Zinks auf elektro-litischem Wege, Gunther, 1904, 99–180 and Die elektrochemische und elektrometallurgische Industrie Grossbritanniens, Kershaw, 1904, 108, and also in Applied Electro-Chemistry, Allmand, 1912, 286

(d) *Proposals and non-important methods for the manufacture of Chlorine*—Many processes have been proposed and tried for utilising the residual ammonium chloride, or the residual calcium chloride of the ammonia soda process, but with the exception of Hopfner's zinc chloride method just previously described, none are now in use. Many other processes have also been tried for preparing chlorine from various sources and in various ways, but have been abandoned. Some of these old methods are enumerated below; fuller information may be obtained from Lunge's Sulphuric Acid and Alkali.

1. *Chlorine from ammonium chloride.*—The most persistent efforts for the direct manu facture of chlorine from NH_4Cl were made by Mond, who took out the English patents: Nos. 65, 66, 1049, 3238, 8308, of 1886; 10955 and 17273 of 1887; 2160 and 2575 of 1889. Articles dealing with the Mond process are found in J. Soc. Chem. Ind. 1892, 466; 1893, 10; and 1893, 63. There was also a proposition from the Verein Chemische Fabriken of Mainz (Eng. Pat. 3322 of 1886).

2. *Chlorine from* $CaCl_2$.—Persistent efforts for the direct recovery of the chlorine in the $CaCl_2$ produced in the ammonia stills of the ammonia-soda process were made by Solvay : Patents 77 and 171 of 1877 ; 838 of 1880 ; 7258 and 7259 of 1884; 8724 of 1885; 13389 of 1886 ; 18574 of 1888. Other patents : Twy nam's process (Eng. Pat. 731 of 1885); Bram ley's process (Eng. Pat. 8289 of 1887); Lyte and Steinhart (Eng. Pat. 21225 of 1890)

Chlorine from magnesium chloride.—Many efforts were made by Weldon to produce chlorine direct from MgCl$_2$; his patents are: Eng. Pt. 565 of 1868; 967, 968, of 1881; Weldon and Péchiney, 9305, 11035, of 1884; 14653, 14654, of 1887. Detailed description of the Weldon-Péchiney experimental plant at Salindre, is given by Dewar (J. Soc. Chem. Ind. 1887, 775). Other patents are: Wilson (Eng. Pat. 3098 of 1885); Gamble (Eng. Pat. 11581 of 1888); Lyte and Tatters (Eng. Pat. 17217 of 1889); Schlosing (Eng. Pat. 11821 of 1887; 11469, 11470 of 1891). (*See also* Eschellmann, J. Soc Chem. Ind. 1889, 2; comp *ibid.* 100.)

Chlorine produced by passing HCl gas over heated peroxide of iron or manganese is the subject of a patent by H Burns (No. 15448 of 1886).

Chlorine by permanganates has been the object of patents by Tilghman (1847), Condy (1866), Tessié du Motay (1871 and 1873).

Chlorine from chromates and HCl has been proposed by MacDougal and Rawson (1848), Pehgot (Ann. Chim Phys [2] 411, 267), Gentele (1861), Shanks (1858), Claus (1867), Aubertin (1873).

Chlorine by heating metallic chlorides with MnO$_2$ and H$_2$SO$_4$ was patented by Binks in 1853.

Chlorine by the assistance of nitric acid or nitrates.—Baggs and Simpson (1864) proposed making chlorine from *aqua regia* Dunlop (1847) patented the preparation of chlorine along with nitrous acid, by heating together common salt, sodium nitrate, and sulphuric acid, the nitrous acid is absorbed by vitriol and the chlorine is passed on to bleaching-powder chambers. This process was working for many years at St. Rollox; it was patented again by Roberts and Dale in 1868; and a patent running on similar lines is that of J. Taylor (No. 13025 of 1884) Other processes employing nitrates or nitric acid, which have not had any practical success, are those of Banks (1839), Tessié du Motay (Bull. Soc. chim. 22, 48), Schlösing (Compt. rend. 55, 284). The later patents are those of Donald, Eng. Pat. 62 of 1887; and Just, Eng. Pat. 14857 and 14859 of 1888; Davis, Eng. Pat. 6416, 6698, and 6831 of 1890; Wallis, Eng. Pat. 13822 of 1892; and Krause, Eng. Pat. 16227 of 1894.

Chlorine Liquid.—Liquid chlorine was first obtained in 1805 by Northmore. The pure gas can be condensed to a liquid at atmospheric temperature, 15°, by a pressure of six atmospheres, or at atmospheric pressure by reducing its temperature to −34°. If the gas is not pure it requires higher pressures or lower temperatures to liquefy it.

The first to prepare it commercially was Knietsch of the Badische Anilin und Soda Fabrik in 1888. The English Patent 13070 of 1888 records that the ordinary metals withstand the action of chlorine gas provided the gas be dry, so that cast iron, wrought iron, steel, phosphor bronze, brass, copper, zinc and lead may be used for making apparatus for dealing with gaseous and liquid chlorine. The resistance of ordinary metals to attack was evidently not sufficient for the manufacture of a pump with moving metallic piston or plunger, for the patent describes two pumps each with a moving piston of concentrated sulphuric acid to confine

and compress the chlorine gas contained in one limb of a U-tube, while the upper part of the other limb contains another liquid like paraffin oil in which pressure is exerted either by an external pump filled with the same liquid, Fig. 20, or an internal plunger A, Fig. 21. In the first figure the gas valves D and C are shown
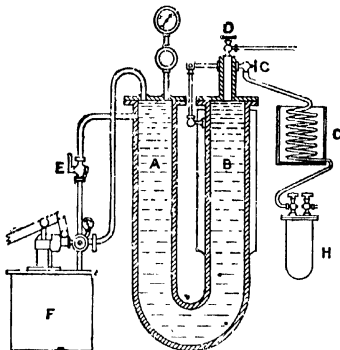
FIG. 20.

external and are actuated by hand In the latter figure the valves are internal and are actuated by their own weight and the pressures of the gas, the inlet valve sits on the top of the pipe F, the outlet valve sits on the top of the pipe opening into the bottom of the chamber D. To ensure that the whole of the gas is swept out of the compression chamber a small pipe with an external controlling valve is arranged between the chamber D and the compression chamber so that on each suction stroke a portion of the acid in D enters the compression chamber along with the gas from F, and on each pressure stroke first chlorine gas and then a little sulphuric acid passes the automatic valve in the bottom of D. To prevent intermingling of the paraffin and acid the pump limb in Fig. 21 is enlarged in diameter at B. To prevent the possibility of gas being liquefied in the compression chambers, these are heated by an external jacket as around B in Fig. 20, and as E,G in Fig. 21. The compressed gas on leaving either form of pump is liquefied in a cooler, as G in Fig. 20, and then runs into the collecting vessel H.
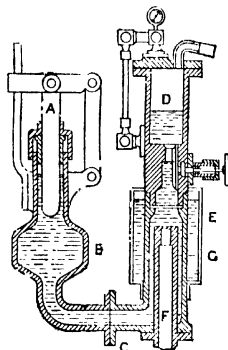
FIG. 21.

In 1909–10 the manufacture was started in the United States of America. With minor

alterations Knietsch's process is still used though it had its difficulties. The Metallurgical and Chemical Engineering of 1916, 1, 215, states that liquid chlorine is now made almost entirely from electrolytic chlorine, and that Deacon chlorine is no good for the purpose unless it is first strengthened, as by extracting the chlorine with stannic chloride as proposed by Goldschmidt. Starting with a gas supply of 97 to 98 p.c. purity the uncondensable blow-off gas still contains 55–65 p.c. chlorine, and this is absorbed in bleach chambers.

As already stated pure chlorine can be liquefied at atmospheric pressure by reducing its temperature to – 34°. The Linde Co., of Germany, have introduced the process of simply cooling the chlorine gas to – 45° without applying any pressure, but they are said not to liquefy so high a percentage of the gas as the older process. In 1911 Blucher's Modern Industrial Chemistry states that it was becoming more and more general simply to cool the chlorine gas in refrigerators so that it liquefied at normal pressures.

The liquid is supplied in steel cylinders or in tank cars holding several tons. The physical properties of the liquid were determined by Knietsch (Liebig's Ann. 259, 100; the Fifth International Chemical Congress, Zeit f Comp u. flussige Gase, 1904, 71), and certain of them have been confirmed by Lange (Zeit f Comprimirte und flussige Gase, 1901, 39), who showed that the thermal coefficient of expansion rises steadily to 88° when its value is 0 00366, that is the same value as is given by ordinary gases, and that above that temperature the liquid expands more rapidly than the gases ; he also showed that whereas liquid chlorine does not act upon iron at any temperature up to 83°, yet at 96° there is a small action ; for these several reasons a cylinder of chlorine filled in the ordinary way begins to become unsafe when heated to 90°.

Applications of Chlorine.—It is used for the extraction of gold from its ores, and much work has been done on its use for extracting copper, lead, and zinc from mixed ores. It is used for converting ferrocyanide into ferricyanides ; manganate of soda into the permanganate, ferrous chloride into ferric chloride, and was used for converting alumina into aluminium sodium chloride ; converting tin into stannic chloride either from pure tin or from scrap tinned iron, after which the residual iron can be again smelted for metallic iron ; this Goldschmidt process of detinning consumed large quantities of chlorine in Germany and led to the preparation of liquid chlorine in the United States of America when a plant in Chicago was installed in 1911 to treat 40,000 tons of tin scrap per year. It is used along with electrolytic hydrogen for preparing hydrochloric acid in Germany and America. It is largely used for purifying drinking water, the liquefied chlorine being extremely handy for this purpose as the supply can be automatically regulated in any proportion to the amount of water passing in the mains ; and a summary of the work done on gaseous chlorine as a disinfectant is given by Clayton (Journ. Soc. Chem. Ind., 1896, 320). When used for bleaching it may be absorbed in caustic alkali to make the corresponding hypo-

chlorite, or it may be absorbed in sodium carbonate solution to make hypochlorous acid ,

$$Na_2CO_3 + Cl_2 + H_2O = HOCl + NaHCO_3 + NaCl$$

which acts approximately twice as energetically as the corresponding amount of neutral hypochlorite.

It is used for converting carbon disulphide into carbon tetrachloride and sulphur chloride, and for preparing the latter direct from sulphur ; for converting benzene into monochlorbenzene, dichlorbenzenes, and trichlorbenzenes, acetic acid into monochloracetic acid, toluene into benzylchloride, benzylene dichloride, and benzyl trichloride, and alcohol into chloral. In all these reactions the hydrochloric acid simultaneously formed is condensed in water and a very pure muriatic acid is thus obtained.

It is combined with acetylene to form tetrachlorethane, and from derivatives of this it is used to form pentachlorethane and tetrachlorethene ; with carbon monoxide it is combined to form carbonyl chloride, with sulphur dioxide it is combined to form sulphuryl chloride (Ullmann, Chemische Industrie, 1908, 405). Other uses of chlorine are for chlorinating anthracene, anthraquinone, the cresols, benzoic acid, the xylenes, isoamylchloride (Perkin, Journ. Soc. Chem Ind 1912, 616), for the preparation of acetyl chloride, and of acetic anhydride.

Many of the above uses of chlorine have been developed because of the necessity of finding new outlets for the enormous quantities of chlorine produced in recent years by the electrolytic processes for preparing caustic potash and caustic soda

The poisonous properties of chlorine gas were first used in warfare by the Germans. In April, 1915, near Ypres, a German deserter in the Ypres salient gave warning of the first attempt to use poison gas in modern warfare. No one believed him ; but a week later the enemy launched his first attack with chlorine gas against our unprepared and unprotected troops. The gas was liberated from cylinders containing 40 lbs. of liquid chlorine. The German war of frightfulness was made to include chemical frightfulness Protection against the chlorine gas clouds was obtained by a helmet consisting of a flannel bag soaked in a solution of sodium thiosulphate and sodium carbonate, and containing a mica window (Bevan, Journ. Soc. Chem. Ind. 1916, 651 ; Self, Journ. Soc. Chem. Ind. 1915, 868). Since then the Germans have used a number of gaseous chlorine compounds as poison gases, as phosgene $COCl_2$, chloropicrin $CCl_3(NO_2)$, trichloromethylchloroformate $ClCOOCCl_3$, "mustard gas" dichlorodiethylsulphide $(CH_2Cl\cdot CH)_2S$, phenylcarbylamine chloride, diphenylchlorarsine, dichloromethylether, chloroacetone, chlorosulphonic acid, methylchlorosulphonate (Journ. Soc. Chem. Ind. 1918, 127 R ; and Tone, Metallurgical and Chemical Engineering, 1918 [2] 357). Shame to their boasted Kultur !

In the following pages are described in detail the applications for the manufacture of bleaching powder, liquid chloride of lime, calcium hypochlorite crystal, potassium hypochlorite solution, sodium hypochlorite solution, sodium hypochlorite crystal, potassium chlorate, sodium chlorate and hydrochloric acid.

Chloride of lime or bleaching powder. By far the greater part of the chlorine produced on a manufacturing scale is converted into *chloride of lime or bleaching powder.*

In 1799 Charles Tennant took out a patent for absorbing chlorine by dry hydrate of lime, and the compound thus formed, 'bleaching powder,' was sold by the St. Rollox Works, established in the same year, at 140l. per ton.

Composition of Bleaching Powder.—This substance being originally supposed to be a direct compound of chlorine and lime received its original name of chloride of lime; but in 1835 Balard propounded the theory that bleaching powder was a compound or mixture of equivalent proportions of calcium hypochlorite and chloride

$$Ca(OCl)_2 + CaCl_2$$
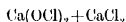
mixed mechanically with a residue of calcium hydroxide.

In 1842 Gay-Lussac supported these views Subsequently Odling, Lunge, Schappi and Naef showed that $CaCl_2$ as such does not exist in bleaching powder, as it cannot be extracted by alcohol, etc, and they therefore proposed the constitution Cl Ca OCl, and the full formula for bleaching powder may then be written $Ca \left\{ {Cl \atop OCl} + H_2O. \right.$ Free lime is always present in commercial bleaching powder because it is only guaranteed to contain 35 p.c of available chlorine, and steps are taken not to let the chlorine exceed this amount essentially, bleaching powder can experimentally be made much stronger than 35 p.c. So much so that any attempt to express the free lime as an essential component is evidently fallacious.

Preparation of Lime for Bleaching Powder.—The lime required for the manufacture of bleaching powder must be from as pure a limestone as possible and must be well burned. Among the most suitable limes for bleaching powder is that used in Lancashire, and made by burning the Derbyshire limestone in the district round Buxton. The average composition of this limestone is:

$CaCO_3$	.	.	.	.	98·9
$MgCO_3$	.	.	.	.	0·29
Fe_2O_3	.	.	.	.	0·17
Insol. etc.	.	.	.	.	0·35
H_2O	.	.	.	.,	0·05
					99·76

The burnt lime was until recently slaked by spreading it on a brick floor, sprinkling it with water and turning it over with a spade till it has completely fallen to powder, after which it is allowed to remain in a heap for 10 hours, and the slaked lime is then passed through a wire sieve of 12-18 wires to the lineal inch by the aid of rotating cylindrical sieves. The operation of hand slaking gives rise to a considerable amount of heat, steam and dust which being unconfined are very trying to the workers, who protect themselves with muzzles and goggles.

For this reason slaking apparatus have recently been introduced whereby the operation is entirely mechanical and the apparatus is entirely enclosed and properly ventilated, so that not only are steam and dust prevented from escaping but labour is also saved.

The slaked lime as used for bleaching-powder manufacture contains about 25 p.c. H_2O, and should not contain more than 2·5 p.c. $CaCO_3$.

The Bleaching-powder Chambers.—The apparatus in which the chlorine is brought into contact with the slaked lime varies with the concentration of the chlorine gas to be treated.

With highly concentrated chlorine gas of 85-90 p.c. chlorine chambers of large size are used, namely of about 6½ feet in height, so that a man can work inside them, of a width of from 10 to 20 feet and more, and up to 100 feet long. Their sides and top are usually made of about 5- or 6-lb. sheet lead, fastened by external lead straps on an external timber framework, exactly like vitriol chambers.

The floor is made of large stone flags, or of coal-tar asphalt, the joint between the sides and the edge of the floor being specially protected by a skirting and asphalt poured behind it.

The chambers are fitted —with doors at each end, so as to ventilate the chamber when it is being charged or discharged (generally made of iron protected by paint); with glass panes in two opposite sides or ends for observing the colour of the gas, with 'lutes' for introducing the gas; with other lutes in the roof of the chambers for the exit of the unabsorbed gases; and with some contrivance for removing the gas remaining at the end of the operation (*v infra*).

Sometimes the chambers are not erected on the ground-level, but upon pillars, like vitriol chambers, leaving about 10 feet of clear space from the ground. In this case the packing of the finished bleach into casks can be done by means of trap-doors in the chamber floor, with wooden hoppers attached underneath, below which the casks are placed, the bleach being pushed down into them from above by means of wooden rakes.

Sufficient slaked lime is wheeled into the chamber to make a uniform layer of 3 to 4 inches, and the piles of lime are then spread by shovel and a big wooden rake with a plain blade from which stick out below two long gauging spikes and with this the lime is very quickly spread into a perfectly even layer of the desired thickness. In order to assist absorption the surface of the lime is drilled into furrows by a rake similar to that described except that the lower edge is provided with deep notches about three inches wide and the same in height; the increased rate of absorption is caused not so much by the extra surface exposed to the chlorine as by the continuous draught of gas through the ridge resulting from the gas in the furrow (chlorine) being heavier than the gas in the ridge (the residual air from the not pure chlorine). The chamber doors are then closed and the joints made gas-tight with lime putty or with a luting made of tar and china clay.

The 'gassing' of the chambers is done either singly or in series, the former being the old method.

The Single-chamber Method.—A small lute in the top of the chamber being opened, the gas connection is opened, and through the small windows the heavy chlorine could be seen

falling to the bottom of the chamber, and there vanishing. As the formation of the bleaching powder proceeds the gas spreads further, forms a layer all over the lime, the layer increases in thickness and presently chlorine begins to issue from the open lute, which must then be closed and the chlorine main connected to another chamber, without however shutting the gas off from the first chamber, which thus continues to receive a certain amount of chlorine. After a short time the gas inlet to the first chamber is closed, and the chamber is left to itself for 12 to 24 hours, when the gas becomes pale in colour or colourless.

It is difficult to get full-strength bleach by one operation ; there is always a superficial crust which greatly hinders the penetration of the gas. It is, therefore, necessary to turn the stuff over with spades, and treat again with chlorine.

The opening of the chamber doors for this purpose was formerly one of the most awkward operations in an alkali works, as a nuisance was caused not only in the works but sometimes at a distance of a mile or two, and on occasion has been so intolerable as to have produced fatal effects The matter is now under the Inspector of Alkali, &c , Works The gas in the chamber must, before any door is opened, be tested by drawing a sample from the exit end at a height of not more than two feet above the chamber floor.

For testing the sample, several kinds of apparatus have been proposed : e g. that of Ballard (21st Report on Alkali, &c , Works, 37 ; 22nd do. 55) and of Stark (J. Soc. Chem. Ind. 1885, 311). Ballard's apparatus consists of a cylindrical glass jar, closed at the top by an indiarubber cork, through which the nozzle of a 4-oz. enema ball (finger pump) passes, as well as an elbow tube reaching down to the bottom. The lower end of this tube is closed at the lamp, so as to leave an opening fine enough for a needle only to pass through. The horizontal branch of this tube is inserted in the side of the chamber at a point about 2 feet from the bottom. When compressing the ball, the air is driven out by a small hole made in the nozzle just above the cork ; this is now closed by the finger, and on relaxing the pressure the ball will expand, and will cause 4-oz. measures—that is, $\frac{1}{2\frac{1}{7}}$ of a cubic foot—of chamber air to enter into the jar and bubble through the test solution contained therein. This is continued till the end of the reaction is indicated by the test liquor turning blue. The liquor consists of 3·485 grams of arsenious acid, dissolved in sodium carbonate and rendered neutral by sulphuric acid, to which is added 250 grains potassium iodide, 50 grains precipitated chalk, 10,000 grains water, 6–10 drops ammonia. For each test 400 grains are used, adding a little starch paste at the time of using. When 2½ grains of chlorine per cubic foot are present in the chamber air, ten aspirations of the chlorometer will cause a blue colour to appear ; if more aspirations are needed, there is less chlorine present, and *vice versâ*. Stark's apparatus attains the same end, not by the finger pump (which is certainly a somewhat rough instrument), but by a gas burette on the Orsat principle.

Another form of apparatus is Fletcher's

Collapsing Gas Sampler, an aspirator shaped like a concertina made with ebonite ends and indiarubber coated cloth sides, into which a measured quantity of sodium arsenite is charged. It is easily carried to the chamber without fear of breakage. An attached rubber tube, a short length of glass tube, both cleaned by recent washing, and a piece of soft luting enable it to be attached air-tight to the chamber. By fully pulling the bellows open one-tenth of a cubic foot of gas is drawn in, and the rubber tube being then closed by kinking, the gas is thoroughly shaken with the solution ; a side opening previously closed with a finger is then opened and the gas expelled into the operator's face, it will probably not smell of chlorine ; further measured quantities of gas are drawn in and shaken until the expelled gas begins to smell of chlorine.

If the test is above 2½ grains chlorine further time must be given for the chlorine to be absorbed, or it must be otherwise removed. The most satisfactory way of removing the chlorine is to dust into the chamber through a luted hole in the top, more or less dry slaked lime either by hand or by Brock & Minton's whizzer (Eng. Pat. 7199, 1886 ; 23 Report on Alkali, &c., Works, 58–60) This machine, on being lowered into the hole, rests in the water of the lute and no chlorine escapes. The hopper of the machine is filled with slaked lime powder and the handle being turned the lime drops slowly towards an attached paddle which is revolving at a high speed inside the chamber, and the large air currents which it sets up in the chamber carry the lime dust to a considerable distance in the chamber, and a very energetic absorption of the chlorine begins instantly. To reach every part of the chamber the machine is lifted out of the hole and carried to one or two other holes and these also dusted. In this way anything up to 2 cwt. of chlorine in a chamber 100 ft. long may be absorbed, and the dust settled within 3 hours.

When it is proved by any of these tests that the air in the chamber contains less than 2½ grains of chlorine per cubic foot, and it is daylight, then the chamber doors may be opened.

After the doors have been opened, and the chamber allowed to ventilate itself a little, the workmen wearing thick flannel muzzles may enter, and with shovels turn the bleach. The doors are then closed, luted, and the chamber gassed again as before described.

Sometimes this must be done even a third time, before the appearance of the product and the laboratory test show it to be finished. To avoid the objectionable turning of the bleach in some British works and generally in Germany and France the layers are made only two or even only one inch.

The Series of Chambers Method.—This method was described in Lunge's Sulphuric Acid and Alkali, 1880, as the only rational one. It was described in the Inspector under the Alkali Acts Report for 1885 as a most important improvement used in a large English works by which stronger bleach was prepared than previously possible and that without losing chlorine or causing a nuisance. It was again described by Jahne of Petrowitz, and the abstract is found in J. Soc. Chem. Ind. 1887, 307.

The series consists of at least three chambers, better four, or even more, and with the Deacon chambers, which are worked on the same method, seven chambers form a series. In the series the gas always enters first into a nearly finished chamber, and the unabsorbed gas passes in succession through other chambers which are further and further removed from being finished until the whole of the chlorine is absorbed and the exit gas is accordingly ' sweet.' The thickness of the layer of slaked lime must be such that the whole of it can be sufficiently chlorinated without turning. When it is considered that the first chamber has been sufficiently chlorinated the stream of strong chlorine is directed into the next following chamber and is cut off from the finished chamber. The finished chamber is, of course, full of chlorine nearly as strong as that supplied by the generators and it is absorbed by the bleaching powder only exceedingly slowly. The easiest and quickest way of removing this gas is by the use of Brock and Minton's whizzer described in the 'single chamber method.' When the chamber is sweetened with all the precautions previously described it may be opened ; the bleach may be very carefully sampled, taking great care to take due proportions of the top and bottom layers, and the sample tested in the laboratory. The experience of the workmen generally leads to the obtaining of a satisfactory test, but should it be low the chamber may be turned or not, closed, and gassed again for a certain time, and then treated as before, and finally the bleaching powder removed. The empty chamber is at once limed, closed, and put into the working series again, but now as the last chamber of the series. Each chamber in turn comes up to strength and is removed from the series, packed, limed and inserted again into the series ; and so on indefinitely. The system of gas pipes and lutes necessary for making these changes is figured in Lunge's Sulphuric Acid and Alkali, 3rd ed. vol. 3, p. 618, for a set of three chambers, and the same system of pipes are used for the Deacon Chambers next described

The following rules relating to bleaching powder chambers worked in either of the two preceding ways are recommended by the Chief Inspector of Alkali, &c., Works (Mr. A. E. Fletcher), in his 21st Report, 12 :—

I. Bleaching-powder chambers should contain not less than 200 square feet of floor space for every ton of powder made in them per week. If there is less space, the work, and especially the packing, must be hurried too much.

II. The chambers should be so arranged and connected together that the residual chlorine from a finished chamber may be drawn into one containing fresh lime, unless some other means be employed for absorbing it (such as Brock and Minton's plan described above). The air finally discharged into the atmosphere or into a flue or chimney must not contain more chlorine than 2½ grains per cubic foot.

III. No chamber should be opened when the air in it contains more than 2½ grains of chlorine per cubic foot. In testing for this, the air should be drawn from a point not more than 2 feet above the chamber floor, and taken from the draught end.

IV. No chamber may be opened until the air

in it has been tested, and the result of such test entered in a book.

V. No chamber may be opened except in daylight.

Mechanical Chambers for absorbing Strong Chlorine Gas.—Many proposals have been made for mechanical absorbing apparatus for strong chlorine, but none of them seems to have met with permanent success ; sometimes the working parts are worn out after a short time, and sometimes the bleach produced in them is too weak. Of course, it cannot be said that the construction of a mechanical chlorine absorber for dry lime is an impossibility, but it must be difficult to construct unless a perfectly regular stream of chlorine gas is at command, and efficient means are employed for artificially removing the heat given off during the absorption.

The absorption of weak chlorine, that is, chlorine diluted with very much nitrogen and oxygen, as it is obtained in the Deacon process, and in most of the processes proposed for dealing with calcium and magnesium chlorides, cannot be carried out in the ordinary chambers. The most efficient plants for this purpose are Deacon's shelf chambers, and Hasenclever's mechanical chambers.

Deacon's chambers, To expedite the rate of absorption the furrowed layer of lime is reduced greatly in thickness, viz. to ⅝ inch. As the weak chlorine contains 90 or more p.c. of inert gases, that is, it contains per unit of chlorine nearly 200 times as much inert gas as does Weldon chlorine, the dilution of the incoming Deacon chlorine by the very large volume of air or residual gases in the Weldon chambers is unnecessary to keep down the temperature of the bleaching powder, and the layer of gas is accordingly reduced greatly in thickness, viz. to about 6 inches. Further, as the escaping inert gases are able to carry away the heat generated, it is unnecessary to have the large heat radiating surfaces which are provided by the Weldon chambers, and it is therefore possible to reduce the ground space occupied by placing as many as sixteen such lime and gas layers as described above over each other. Chambers only 6 inches high cannot, of course, be charged with lime and discharged of their bleach by workmen entering the chamber as with the Weldon chambers, but must be operated by the workmen from outside the chambers with long-handled rakes, which, from the hygienic point of view, is a great advantage.

Figs. 22 and 23 show the construction of a set of seven Deacon chambers, Fig. 22 being a front elevation of 3¼ chambers, and Fig. 23 being a view of the broken end shown by Fig. 22 ; the dimensions of each chamber are 8 feet wide and 13 feet high, as shown by Fig. 22, and 21 feet long and 13 feet high, as shown by Fig. 23. Each chamber is subdivided into two halves by a central partial partition, as is shown by the right-hand side of Fig. 22, but the figures do not show the gas passage which exists through the bottom of these partial partitions, nor do they indicate that the gases flow downwards in each left-hand half, and flow upwards in each right-hand half, chamber. The partitions and partial partitions are made of slate or sandstone flags, and they are carried by the pillars and girders shown in

the figures. The partitions and partial partitions in turn carry the sixteen shelves to support the lime layers, and also carry the top covering shelves. The shelves are made of slate or flagstone; the bottom and top slabs only reach to each end of the chamber, all other slabs end 6 inches short of one or other end of the chamber to allow the gases from the inlet pipe to zigzag down the one half of the chamber, as shown by Fig. 23, and then zigzag up again on the other half of the chamber to the outlet pipe; all the shelves have a gap of a foot in the middle of the 21-foot dimension, and these gaps are covered by easily removable boards, as shown by B and C in Fig 23. To lime the chamber the wooden covers B are removed, and the wooden slides C are pushed on one side with the exception of the two on the bottom shelves. Sufficient lime to cover one shelf with a layer nearly 1 inch thick is then dropped through the gaps from which the covers B have been removed, and falls down to the two bottom shelves. There it is spread and then furrowed by long-handled rakes from each end

of the chamber. The slides C on the bottom shelf but one are then pushed over their gaps, and the lime charges for those shelves dropped and levelled as before. The rest of the shelves are limed similarly till all are limed, and the top gaps covered with their boards B and made gas-tight with lime or with luting. The ends of the chamber are closed by hanging iron plates on the shelves, as shown on the left side of Fig. 22; the joints are made gas-tight with luting. Each of the other six chambers is limed similarly. The two top cover flags of each chamber each contain a hole provided with a water lute, the left one serving as inlet, the right one as outlet to the chamber. The gas supply main is shown in Fig. 22, with a lute for each of the seven chambers, and the movable arm is shown in position which passes the gas into the first chamber. The exit gas from the first chamber passes into the second chamber, and all following chambers in turn by movable arms, shown in Fig. 22 and in Fig. 23, where one arm is marked A. From the seventh chamber the exit gas passes by an arm into the middle or exit main
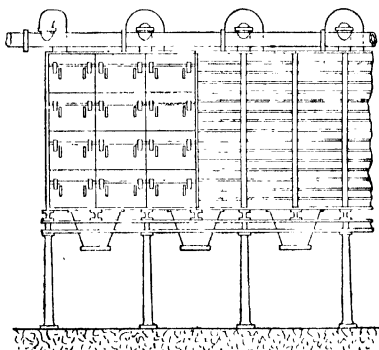
FIG. 22.
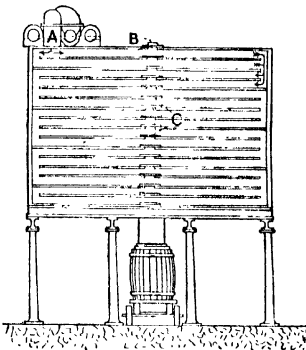
FIG. 23.

shown in Fig. 23, whence it is sucked by a fan, and being now free from chlorine, is blown into the air; the exit main runs the whole length of the chambers, and is provided with a lute adjacent to the exit lute of each chamber When samples taken through test holes in the end covers show that the bleach is up to strength, the gas arms are changed, so that the gas supply is cut off the first chamber, and then goes to the second, and thence, as before, to the seventh. The finished bleaching powder in the first chamber is discharged by removing the end doors, pushing on one side the slides C, and then pushing the bleaching powder to the centre of the chamber, where it falls through the gaps and the hopper shown in the figures into the cask below. The chamber is next relimed, and the ends closed as before described, and it is ready to become the last chamber in the series. To effect this the exit from the seventh chamber is cut off from the exit main, and instead it is joined by a gas arm to the right-hand main shown in Fig. 23, which return main carries the gas the whole length of the chambers, and by a suitable arm is connected to the inlet

of the first chamber. The exit from the first chamber is connected to the exit main. Each chamber in turn is thus discharged, relimed and reinserted into the cycle. Such a set of chambers furnishes 4 tons of bleach per day.

Hasenclever's chambers.—Another style of chamber which is particularly suitable for absorbing weak chlorine such as is produced by the Deacon process, is the mechanical chamber of Hasenclever (Eng. Pat. 17012, 1888), employed at Aachen, and strongly recommended by an English Commission as a thorough remedy of the difficulty arising from the contact of the workmen with the chlorine gas and the bleaching powder dust connected with the use of the Weldon chambers. To make these Hasenclever chambers suitable for use with strong chlorine they may be worked intermittently, and it has been proposed to make them suitable by mixing air with the chlorine. The Figs. 24 and 25 show one of the original forms of the apparatus. Fig. 25, in its central portion, is an elevation, but in its upper and lower portions is a sectional elevation, and in several respects is very indistinct; Fig. 24

shows on the left side an elevation of the back ends of the tubes, while on the right side it shows the front ends of the tubes with the covers removed that carry that end of the shafts. The slaked lime passes from the hopper shown in both figures into the top tube, where it is slowly worked by the blades attached to the revolving shaft towards the back end of the tube, where the first and second tubes are united by a large passage not adequately shown in Fig. 25. The direction of rotation and the setting of the blades in the second tube are such that the lime is now slowly moved along the second tube towards its front end, where it drops through another large passage into the third tube; from the back of the third tube it drops again into the back of the fourth tube, and finally at the front end of the fourth tube drops into the hopper, which is closed by a sliding door. The chlorine enters at the front of the fourth tube and passes to the tubes above

by the large passages already mentioned, and the residual gases escape from the front end of the first tube as shown, to the suction fan actuating the whole Deacon plant. Fig. 25 shows four circles at the back ends of the tubes and two circles at the right ends of the tubes, and Fig. 24 shows two gas passages on the middle tubes, which are antiquated, and should not have been shown. By gently drawing the slide of the hopper the bleach falls direct into the cask with practically no nuisance. Means are provided at the back end of the fourth tube of easily starting or stopping the shafts. and doors are provided for inspecting and, when necessary, cleaning the inside of the tubes, as shown by Fig. 25, for second and third tubes. and by Fig. 24 right-hand side for all four tubes Such a set of tubes makes 1 ton bleach per day.

General Remarks on the making of Bleaching Powder.—Good strong bleach cannot be made
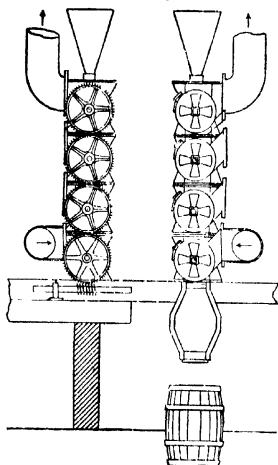
FIG. 24.
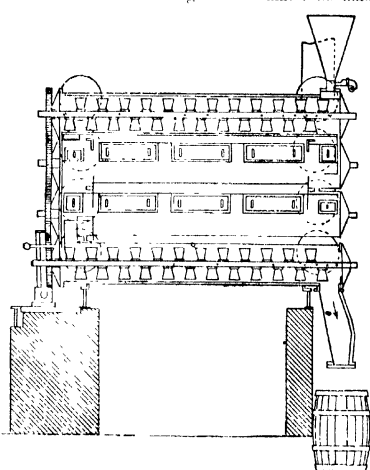
FIG. 25.

from lime that is badly burnt, slaked, or sifted, nor from chlorine that contains too much carbon dioxide or aqueous vapour or hydrochloric acid gas, nor in very hot weather, nor if the chlorine is initially passed into the chamber so fast as to allow the temperature to rise too high. It ought to consist of pretty heavy flakes, easily crushed, or a heavy but not dusty powder, which can be kneaded with the fingers into a tough paste. The laboratory test of a sample carefully taken from various parts must test at least 35 p.c. available chlorine, and if it is intended for export it must test still higher.

Packages.—Bleaching powder must be packed in very well-made casks, preferably made of hard wood. The ends are sometimes secured by a coat of plaster of Paris. This is done in order to prevent the access of air, which quickly deteriorates the powder both by its moisture and its carbonic acid.

The packages must be kept in cool, dry

places; both rain and sun would quickly spoil the bleaching powder, even if placed in good casks.

Properties of Bleaching Powder. — Good bleaching powder is a nearly white powder, often mixed with lumps which, however, test as high or even higher than the powder. It has a peculiar smell, quite different from that of chlorine, and not owing to hypochlorous acid, since it is just as perceptible in alkaline solutions. If it gets on to the skin a very strong odour is developed, which is highly characteristic; this odour persists even after washing the skin with soap.

In the air bleaching powder attracts moisture and carbonic acid, and gradually changes into a pasty mass. Mixed with a little water, it forms a stiff paste, with a perceptible swelling and rise of temperature; this is probably caused by the transformation of $2CaOCl_2$ into $Ca(OCl)_2$ and $CaCl_2$, which then acts upon the

free lime to form crystals of calcium oxychloride which causes the mass to set like cement.

Bleaching powder decomposes gradually even in closely stoppered bottles or well-protected casks. The presence of light, heat, moisture, and carbonic acid greatly accelerates this change ; so does shaking, *e.g.* in transit. Hence the strength of bleach is usually only guaranteed at the place of shipment, but it ought not to lose above 2 or at most 3 p.c. by a few weeks' journey.

Experiments on the rate at which bleaching powder loses its available chlorine have been made by J. Pattinson, in 1874 (Chem. News, 29, 143) and 1886 (J. Soc. Chem. Ind. 587). He experimented in the first case with samples kept in loosely corked bottles, sheltered from direct sunlight, and found that these lost on an average 0·33 p c. monthly from February to April, 0·86 from June to September, 0·28 from November to January. The greatest loss occurred in August, viz. 1·4 p.c. per month.

The keeping properties of bleaching powder depend on the quality of the lime used, on the temperature conditions under which it has been made, and on its strength. The more free calcium hydroxide is left in the bleaching powder, the more stable it is. This shows that, when bleaching powder is required for export, especially to tropical countries, it is a mistake to require a high initial test.

A few experiments made by Thummel (Arch. Pharm. 1834, 22, 1) prove that light has much more action on bleaching powder than exposure to air.

The following complete analyses of the samples of bleaching powder investigated by J. Pattinson (*v. supra*) may serve as an example of the best descriptions of the commercial article :—

	A made of Irish limestone (from Larne)	B made of Irish limestone by another manufacturer	C made of French cliff
Available chlorine . .	37·00	38·30	36·00
Chlorine as chloride .	0·35	0·59	0·32
Chlorine as chlorate .	0·25	0·08	0·26
Lime	44·49	43·34	44·66
Magnesia . . .	0 40	0 31	0·43
Ferric oxide . . .	0 05	0 04	0·02
Alumina . . .	0·43	0·41	0·33
Oxide of manganese .	trace	trace	trace
Carbonic acid . .	0·18	0·30	0·48
Siliceous matter . .	0·40	0 30	0·50
Water and loss . .	16 45	16 33	17·00
	100 00	100·00	100·00
Total chlorine . .	37·60	38·97	36·58

The following are analyses of bleaching powder made by Lunge and Schappi, from perfectly pure lime and with the greatest care, so as to obtain the strongest possible product :—

Available chlorine . . .	43·13
Chlorine as chloride . .	0·29
Lime	39·89
CO$_2$	0 42
H$_2$O (direct estimation) . .	17 00

Calculated as :

CaOCl$_2$ + H$_2$O . .	88·08
CaCO$_3$	0·96
CaCl$_2$	0·45
Ca(OH)$_2$	6·74
H$_2$O not combined . .	3·77
	100·00

The small quantity of unchanged calcium hydroxide is proof for the opinion that this is merely lime mechanically protected against the action of chlorine by the bleaching compound CaOCl$_2$ previously formed.

Liquid chloride of lime or **Bleach liquor.** This substance was first prepared in 1798 by Chas. Tennant by absorbing chlorine gas in milk of lime. Many bleach works have prepared it on quite a small scale for their own use, but it is now prepared by alkali works on a considerable scale for use in bleach works in the not too distant neighbourhood, packed in carboys or steel tank wagons, as being more convenient than the preparation of clear solutions of bleaching powder by the bleach works.

Absorption of Chlorine by Milk of Lime.— As all the processes for preparing chlorine on a commercial scale produce it at approximately atmospheric pressure, the gas has to be absorbed by the surface of the milk of lime, and because of the very small solubility of lime in water agitation of the milk of lime is an absolute necessity to keep the lime in suspension and to accelerate its solution, and to bring the lime solution to the surface, and after it has absorbed its modicum of chlorine, to quickly remove it and again saturate it with lime. Various forms of agitators have been used : blades attached to horizontal shafts, or to vertical shafts, or to vertical revolving cones or cylinders, and these last are considered to be the most efficient, as, besides setting up a swirl in the liquid, they also set up a very rapid flow of liquor from the bottom to the top, thus very effectually and rapidly renewing the surface of the liquor.

The containing vessels have been made of lead, or flagstone, but cast iron is now employed, as it soon becomes coated with a limey deposit

both below and above the liquor, and any action of the gas or liquor is reduced to a minimum. Three or more vessels are coupled up so that the gas passes them in series. Each is filled with water and lime in the proportion of 100 gallons and 10 to 15 lbs., making a milk of 12° to 18°Tw. During the absorption of the chlorine the temperature rises, and the admission of the chlorine should be so regulated that the temperature does not rise above 32°, or at most 37°, and for this same reason the absorbers may be cooled by building them inside a water tank. When the sp.gr. of the liquor after settling clear has risen to 1·040, or the contents of available chlorine is 7 p c., the gas is passed into the next absorber as first in the series, and the first absorber is allowed to settle the considerable amount of excess lime which is absolutely essential to prevent the conversion of the hypochlorite into chlorate. The clear liquid is then run off into carboys. The residual lime is either augmented with some fresh lime for the next operation, or if the accumulated impurities in it are too great, it is washed to recover admixed hypochlorite, and is then run away.

Dissolving Bleaching Powder to make Bleach Liquor.—When bleach liquor cannot economically be obtained from the source just described, it is always prepared by the bleaching works by extracting bleaching powder with water. To avoid a loss of available chlorine and a waste of time in settling out the insoluble matter, certain conditions have to be observed, so that it cannot form lumps inside the dissolver.

1. The best practical temperature for the water is 21° to 26°.

2. The agitation must be effected by mechanical power so as to show a strong swirl on the surface, say, with a peripheral speed on the agitator of 500 feet per minute for tanks of 5 feet to 9 feet diameter, and the lower limbs of the agitator must be not more than 1 inch from the bottom of the tank.

3. The bleaching powder must be emptied a little at a time on to a 1-inch mesh sieve placed outside and above the dissolver, and the passage of the powder assisted by working it with a spade, any lumps then left are to be knocked through with the flat of the spade. After completing the bath, agitation for 20 minutes is ample for all strengths of solution up to 16°Tw. Further time spent on agitation is wasted, and, by beating the insoluble residue, renders subsequent settling appreciably slower.

4. The run-off pipe should be at such a height as to allow 5 cubic feet of sludge per cwt. of bleaching powder used per batch, for all strengths of solution up to 16°Tw. Unless a sufficient space is allowed, enormous waste of time will arise in waiting for the last few inches to settle clear.

5. The residual sludge consists, not of bleaching powder, but of insoluble lime suspended in bleach solution. The agitating tank should be filled again with water, and the contents agitated for 5 minutes only prior to settling, when the clear liquor of about 2°Tw. is run off to be used for making the next batch, and the washed sludge is then to be run away to waste.

When the precautions given above are followed, the loss of bleaching powder in the washed sludge will not exceed 2 lbs. per cwt. of bleaching powder used.

Properties and Uses of Bleach Liquor.—The experiments made by Lunge and Landolt (J. Soc. Dyers and Colorists, 1885, Nov. 25) with bleach liquor have shown that the action of the air is nothing like so injurious to the stability of such solutions as that of the light, which ought to be excluded by all means. Solutions kept in the dark in closed vessels, remained practically unchanged up to the 24th day, and up to the 33rd day, when the experiment was finished, the strength had only decreased from 29·58 to 29·12. Kept in open vessels in the dark, they remained unaltered up, to the 12th day; on the 33rd day they had lost 3·30. But when kept in closed vessels in diffused daylight, the decomposition set in at once, and on the 33rd day only 8·52 remained of 33·02 originally present. Solutions of chloride of magnesia behaved similarly to those of chloride of lime; those of zinc or aluminium hypochlorite, as might be expected, were much less stable.

The specific gravity (at 15°) can be used to approximately determine the available chlorine grams per litre in a good bleach liquor

Sp gr		
1 01	. .	5·58
1·02	. .	11·41
1 03	. .	17·36
1·04	. .	23·75
1·05	. .	29·60
1·06	. ⌐	35·81
1·07	. .	42·31
1·08	. .	48·96
1·09	. .	55·18
1·10	. .	61·50

but such a method is utterly useless for an old solution, or one that has been partly used, or is in any other way abnormal; the only way of testing such an abnormal solution is to make a chemical test, the best of which is Penot's method, with sodium arsenite in presence of bicarbonate of soda (Lunge and Hurter's Alkali Maker's Handbook, 2nd ed 126).

The use of bleach liquor for bleaching purposes is described in Cross and Bevan's Cellulose, 2nd ed. 284–294. The effect of free lime on bleaching is similar to that of free caustic soda when sodium hypochlorite is employed for bleaching.

The germicidal power of bleaching-powder solution is very great, and it has been used successfully for years as a disinfectant. One part of bleaching powder will, in 2–4 hours, destroy the following bacteria : coli, typhosus, and cholera in 2000 parts of ordinary sewage.

(*See* Schumacher, in Gesundheit-Ingenieur of Munich and Berlin, August 10, 19, 30, 1905 ; Sheridan Delépine, in Medical Chronicle, May, 1894 ; and G. C. Clayton, in J. Soc. Chem. Ind. 1896, 320.)

Calcium hypochlorite crystal. The Chemische Fabrik Griesheim Elektron (D. R. P. 188524, 1906) describes the production of calcium hypochlorite as follows :—

Chlorine is introduced continuously with agitation into milk of lime until the latter is nearly saturated. The solution is then concentrated *in vacuo* until the calcium hypochlorite crystallises out and can be dried *in vacuo*. The calcium hypochlorite obtained is said to be more

stable than ordinary bleaching powder, gives a clear solution in water, and contains 80-90 p.c. available chlorine.

Potassium hypochlorite solution (*Chloride of potash* or *Eau de Javel*). This liquor was first made in 1789 at the Javel Works near Paris, and was the first bleaching compound known. It was then made by passing chlorine into a solution of potashes (crude potassium carbonate) in eight parts of water. This liquor is rarely made at the present time, as it has been replaced by the cheaper soda compound, which has now mostly usurped its name.

Sodium hypochlorite solution (*Eau de Labarraque*, usually called *Eau de Javel*). This liquor was made by passing chlorine into a solution of sodium carbonate in 10 parts of water till the liquid began to effervesce and to bleach litmus

$$Cl_2 + 2Na_2CO_3 + H_2O = NaOCl + NaCl + 2NaHCO_3$$
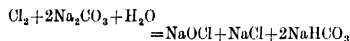
any further passage of chlorine produced free hypochlorous acid and CO_2

$$NaHCO_3 + Cl_2 = HOCl + NaCl + CO_2$$
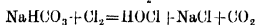
The liquors containing free HOCl keep very badly, the HOCl partly volatilising and partly losing its oxygen.

Hypochlorite of soda solution is used to-day as a bleaching agent for the bleaching of special fabrics, in steam laundries to whiten clothes, and as a disinfectant, and is now prepared by one of the three following methods.

1. By the precipitation of a solution of bleaching powder by sulphate or carbonate of soda, when a solution is obtained containing about 5 p.c. of available chlorine, but no free HClO, and which will, therefore, keep unchanged for some time. This operation is usually conducted at the factory or the place where the solution is used

2. By passing chlorine into a solution of caustic soda until nearly all the soda is chlorinated

$$Cl_2 + 2NaOH = NaClO + NaCl + H_2O$$

This solution is made at alkali works, and sold at a strength of 10-15 p.c. available chlorine.

It has been found necessary to leave a small amount of free caustic soda, about $\frac{1}{2}$ p.c. Na_2O, in order to make the solution stable, by removing all free hypochlorous acid and by removing traces of iron which would otherwise be converted into sodium ferrate, and aid the decomposition by carrying oxygen from the hypochlorite to the atmosphere. A very full statement on the manufacture and stability of sodium hypochlorite solution made in this way is contained in a paper by Muspratt and Smith (J. Soc. Chem. Ind. 1898, 1096).

3. By electrolysis of brine solution. Under chlorine we have discussed the electrolytic cells devised to liberate chlorine from common salt solution. In the case of the preparation of sodium hypochlorite there is no necessity when the electrolysis starts to attempt to keep the main products, chlorine and caustic soda, apart, but, on the other hand, they must be brought together. But directly the formation of hypochlorites has begun then troubles begin : (1) there is insufficient agitation to bring the caustic soda to the chlorine, and consequently chlorine escapes, and free hypochlorous

acid and chlorate are formed ; (2) the hypochlorite, hypochlorous acid and the chlorate are themselves electrolysed with evolution of oxygen, and the output of hypochlorite rapidly falls to nothing ; (3) the hydrogen liberated at the cathode reduces the hypochlorites already formed, and again the output ceases.

The following cells have been introduced (*see* papers by W. H. Walker in Electro-Chemical Industry, 1, 439) :—

The Kellner cell consists of a stoneware vessel divided into a number of small compartments by glass plates fitting into small grooves in its sides. These glass plates are wound with platinum-iridium wire, and form bipolar electrodes. The electrolyte is circulated rapidly through the cell and through a cooling coil.

The Schuckert cell is a large stoneware trough, separated into 8-10 compartments. In these compartments are bipolar electrodes in the making of which platinum-iridium wire may or may not be used. Circulation is effected by means of the hydrogen evolved, and each cell has a cooling coil.

The Haas-Oettel cell consists of a rectangular box divided into small compartments by a series of vertical bipolar carbon electrodes set in grooves.

From the figures given by Walker, the k.w.h. per ton available chlorine produced in solution can be calculated, and are given in the following table for the Kellner and Schuckert cells. The Haas and Oettel figure is taken from a paper by Reuss before the Society of Dyers and Colorists, Feb. 1911 :—

Name of cell	Details of a standard sized cell		K.W.H. per ton available Chlorine
	Amps.	Volts	
Kellner . .	120	110	8800
Schuckert .	100	110	8500
Haas and Oettel	80	110	8400

These cells are adapted for the production of weak solutions only of hypochlorite of soda containing 1-2 p.c. available chlorine, as only a partial decomposition of the NaCl is possible without an enormous fall in efficiency. The cost of salt is, therefore, high, and actually about 7 tons of salt are required per ton of available chlorine produced.

Cells such as these are designed for the purpose of erection at the factory or works where the hypochlorite solution is used, and where neither bleach liquor nor bleaching powder are readily available.

Full details of these and other cells are to be found in the series Monographien über Angewandte Elektrochemie, namely, vol. 8, Engelhardt, Theoretical Constructive Description, 1903, 275 ; vol. 17, Abel, Theoretical Description ; 1905, p. 110 ; vol. 38, Ebert and Nussbaum, Practical Applications, 1910, p. 367, all under the title, Hypochlorite und Elektrische Bleiche.

Uses of Sodium Hypochlorite Solutions.— The uses include the bleaching of such cotton

and linen fabrics as require to have the softest possible feel, and the fullest degree of whiteness; for bleaching paper pulp; for whitening clothes in steam laundries; for disinfectant purposes. Hypochlorite of soda solution possesses strong germicidal powers, which Klein estimates for a solution containing 10 p.c. by weight of available chlorine at 21 times that of phenol. (*See* Klein, Comparative Bacteriological Report on Chloros, Public Health Engineer, June 9, 1906. Also for further data, *see* Schumacher, Gesundheit Ingenieur of Berlin and Munich, Aug. 10, 19, 30, 1905; Clayton, J. Soc. Chem. Ind 1896, 320) And lastly, the strong solution prepared by method 2 is used in enormous quantities by the Badisch Anilin und Soda Fabrik for the conversion of phthalimide into anthranilic acid, which last is used in the manufacture of artificial indigo (Haller, Les Industries chemique et pharmaceutiques, Exposition Universelle de 1900, Paris, vol. 2, pp. 128-130).

Sodium hypochlorite crystal. Until recently sodium hypochlorite in the solid form was unknown. Muspratt and Smith, in 1898, however, by the systematic production of a more and more concentrated solution, produced crystals of the following composition (J. Soc. Chem. Ind. 1898, 1100) :—

NaOCl	.	.	.	37·6 p.c.
NaClO₃	.	.	.	nil
NaCl .	.	.	.	3 7 ,,
Water (by diff.)	.	.	.	58·7 ,,
				100·0

The crystals dissolve in their water of crystallisation at 18°-21°, and then rapidly decompose. By drying under vacuum part of the water of crystallisation is removed, and a more stable product obtained containing up to 60 p.c. of available chlorine with a melting-point of over 43° (*see* Muspratt, J. Soc. Chem. Ind. 1903, 592).

Magnesium, Zinc, and Aluminium Hypochlorites, all of them obtained by adding the sulphates of these bases to a solution of bleaching powder, are sometimes used for special purposes because they have a more rapid action than chloride of lime. Their properties have been fully investigated by Lunge and Landolt in the above-mentioned memoir. They are never manufactured for sale, but prepared by the users themselves.

Potassium chlorate. This salt was originally made by saturating caustic potash solution with chlorine gas. Liebig proposed to saturate a thin paste of three molecules of slaked lime with one molecule of potassium chloride; there is, however, a disadvantage in that some potash is lost along with the insoluble impurities of the lime, and this is obviated by saturating milk of lime only, drawing off the clarified calcium chlorate liquor, evaporating it to the necessary concentration, adding potassium chloride equivalent to the calcium chlorate present, and cooling the solution to crystallise the potassium chlorate. This manufacture was started in 1847 at St. Helens, at Messrs. Muspratt's works, and was described in detail by Jurisch in 1888, Die Fabrikation von Chlorsaurem Kali und Anderen Chloraten, and in Lunge's Sulphuric Acid and Alkali. The absorption of chlorine by milk of

lime begins with the formation of calcium hypochlorite, as has already been described under the heading Liquid Chloride of Lime or Bleach Liquor, and that description applies here, and is supplemented by Fig. 26, the sectional elevation of an absorber built up of cast-iron plates
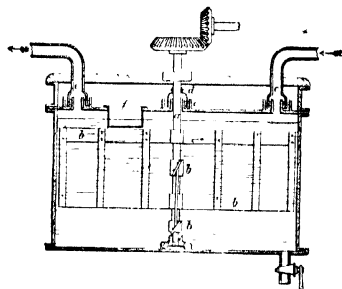
Fig. 26.

with rust cement joints, and 10 feet diameter and 5 feet 6 inches deep; the agitating shaft a with its arms b, b is carried by the foot step, and by the bearing attached to the iron girder seen just below the crown wheel, but this girder does not cover the entire top of the tank or prevent access to the manhole f, as the figure suggests; the device of a cup d and a water lute e prevents any escape of chlorine through the shaft hole. The manhole is always open, so that there is no hindrance to the addition of water or lime or the removal of samples. Sometimes a water-jacket surrounds the absorber to prevent too high a temperature, as described later At least three, better six, absorbers are worked in series on the chlorine, so as to absorb the whole of the chlorine supplied and to obtain an innocuous residual gas; the gas mains for this purpose are not shown in Fig. 26, but they are exactly like those indicated in Figs. 22 and 23.

The milk of lime is also of approximately the same strength as when making bleach liquor; it should not exceed 16° or 17°Tw., which corresponds to 6·3 to 6·7 lbs. CaO per cubic foot.

As the absorption proceeds the temperature slowly rises, and while an excess of lime still remains, the reaction is

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O$$
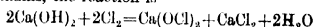
and the temperature should not be allowed to rise above 32° or at most 37°. The reason for keeping the temperature to this limit is that, as the calcium hydrate goes more and more into solution, the impurities that originally accompanied it are more and more released, and become active catalysts, enabling the hypochlorite to decompose $Ca(OCl)_2 = CaCl_2 + O_2$, and this catalytic action is the more active the higher the temperature; the principal impurities acting in this way are the iron and the manganese oxides. The evolution of the minute oxygen bubbles in the turbid liquor causes the formation of a very strong and persistent scum which partly or almost completely covering the surface of the liquor forms so effective a

separating layer between the chlorine gas and the alkaline liquid below that absorption of the gas is very greatly reduced or even entirely stopped. When absorption of the chlorine has gone a little further, so that the free $Ca(OH)_2$ has been acted upon and only remains in small local particles, a series of complicated reactions occur which are not correctly understood, but may possibly be:

$$2Ca(OCl)_2 + 4Cl_2 + 4H_2O = 2CaCl_2 + 8HOCl$$

i.e. a small amount of free hypochlorous acid is formed which, however, has no effect on the remainder of the hypochlorite, but which when further treated with chlorine yields, it is assumed, chlorine monoxide

$$4HOCl + 4Cl_2 = 4Cl_2O + 4HCl$$

and it is assumed that it is this chlorine monoxide which oxidises the hypochlorite to chlorate $Ca(OCl)_2 + 4Cl_2O = Ca(O_3Cl)_2 + 4Cl_2$, with regeneration of the free chlorine. The sum total of these reactions is

$$3Ca(OCl)_2 = Ca(O_3Cl)_2 + 2CaCl_2.$$
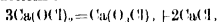
The last reaction is accompanied by the generation of so much heat that the temperature of the liquor rises exceedingly quickly up to 65°–70°, when the scum previously mentioned disappears, as there are no longer any hypochlorites to decompose with evolution of oxygen, and as the reaction of the liquid has changed from alkaline to acid the basic oxides in the scum pass into solution, the liquid smells of chlorine, and the dissolved hypochlorous acid bleaches litmus paper instantly; and lastly, the liquid generally has turned from colourless or light yellow to deep pink, due to the conversion of the manganese in the lime into a permanganate. By summing the equations representing the formation of the hypochlorite and the conversion of the same into chlorate, the total reaction appears

$$6Ca(OH)_2 + 6Cl_2 = Ca(O_3Cl)_2 + 5CaCl_2 + 6H_2O$$
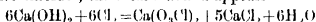
which, though expressing the main end result, fails to represent any of the indispensable intermediate stages. The completion of the conversion of the hypochlorite into chlorate may be readily ascertained by adding to a sample of the cooled liquid some strong hydrochloric acid, there should be no evolution of chlorine gas. Full analysis of the liquor always shows that the molecular proportion of chloride is somewhat greater than indicated by the general equation above, namely 5·0; if much oxygen is evolved the figure may reach 5·8, but with very good work the figure may be 5·3. The operation lasts from less than 24 hours to 72 hours, according to the speed at which the chlorine can be passed so as to comply with the condition of complete absorption. With reference to the possibility of increasing the speed of absorption, and so with efficient cooling reducing the catalytic decomposition of the hypochlorite a description by Lunge (Sulphuric Acid and Alkali) of the absorbing apparatus used by Messrs. Péchiney at Salindres is of considerable interest, the agitation being effected by means of a paddle wheel with horizontal and submerged axis, but each blade in turn projects through the liquid surface as the paddle revolves, and the absorption is excellent and superior to that in all other absorbers.

The finished liquor in the absorber may show, according to the quality and the quantity of the lime used, a strength of from 24°Tw. up to 32°Tw., and statements have been made of strengths obtained up to 44°Tw. To obtain the subsequent separation of the potassium chlorate in a proper manner, it is concentrated by evaporation until it shows from 50°Tw. to 70°Tw., and during the evaporation there is considerable corrosion of the pans and also decomposition of the chlorate. For these reasons it would appear that more attention might be given to the direct manufacture of stronger chlorate liquors by an adaptation of the process referred to by Lunge as used by the Griesheim-Elektron Company for preparation of solid crystalline hypochlorite of calcium.

The finished liquor in the absorber smells of chlorine and of hypochlorous acid, and these objectionable substances for the subsequent treatments may be removed by the addition of small quantities of sodium thiosulphate or of tank waste.

The liquor is run from the absorber into a settling tank, whence the clear liquor is drawn through a deep siphon, and the residual mud is run into a filter press, or is diluted and washed by decantation, the washings being used for making fresh milk of lime.

The strong settled liquor is measured and tested for its content of chlorate, and the theoretical quantity of muriate of potash calculated, allowing for the approximately 5 p.c. of impurities contained in it.

The open boiling-down pans are made either of cast iron or preferably of wrought iron, as it does not crack, and is repairable when damaged by corrosion. After charging with the settled liquor the fires are lighted and the muriate of potash is added. The boiling is continued until the hot liquor shows 70°Tw., when the boiling is stopped and the liquor allowed to settle. The mud consists of magnesia originally contained in the lime, or in the muriate of potash, then converted into chloride which, decomposing in the pans into magnesia and hydrochloric acid, makes a very objectionable mud, and also corrodes the pan from which a sediment of ferric oxide results; the mud also contains gypsum from the original lime, and from the sulphates in the muriate of potash; to prevent this mud from burning fast to the pan it must be removed after each operation, and the soluble salts recovered by washing.

The coolers for the first salts are generally made of iron, since in no case can a pure product be obtained at this stage. They are best made like those used for soda crystals, with a plughole for running off the mother liquor. They ought to be numerous enough to permit of the liquor remaining in them 9 or 10 days in winter and 14 days in summer. Here the crude chlorate of potash crystallises in long acicular crystals, totally unlike in general appearance the thin plates in which the same salt crystallises when pure, but in reality possessing exactly the same crystalline faces, only developed in different fashion. They are easily distinguishable from the large transparent prisms of hydrated calcium chloride which appear if the concentration has been too great. They must be broken up after draining, and the adhering mother liquor washed

off with a little water, and finally drained in a hydro extractor.

The mother liquor is a nearly saturated solution of $CaCl_2$, with a little KCl, and with about 30 grams of $KClO_3$ per litre. With bad work much more chlorate is left in the liquor. In the very best case 10–12 p.c. of all chlorate manufactured is lost through this cause, usually much more (25–30 p.c.). Usually it is not even attempted to recover the chlorine from these liquors by heating with hydrochloric acid—they are simply run to waste. But, with due care, the mother liquors can be quite well worked for chlorine by taking care to run the hydrochloric acid in *pari passu* with the liquor. Strictly speaking, it is not the chlorine of the chlorate which is recovered in this way, but chlorine produced by oxidation of the HCl added.

Wylde, Hammill, and Auer (Eng. Pat. 15097) describe a process for the recovery of about half the chlorate left in the mother liquor by refrigeration. The process is described in detail by Hammill (J. Soc. Chem Ind 1889, 168), who states that the crude crystals obtained by refrigeration have a finer grain than the ordinary crude crystals, but when thrown down from mother liquors of not over 72°Tw., are no more impure, and are as readily refined by one recrystallisation. Hammill says that on cooling to $-12°$ only 13 5 grams $KClO_3$ per litre remain in the liquors. This process has now been worked successfully for many years.

Another process for greatly reducing the loss of chlorate in the mother liquors is that of Péchiney (cf. Weldon, J. Soc Chem. Ind. 1882, 41). He concentrates ordinary chlorate liquor made from lime of a density of 42°Tw., up to 100°Tw. (hot), and cools it down to at least 12°C., but not below 10°C. Of its 5 5 mols. of $CaCl_2$, 4 3 are thus caused to crystallise out as $CaCl_2,2H_2O$ (probably it should be $6H_2O$), but if the temperature were allowed to fall below 10°, calcium chlorate would crystallise as well. The crystals are separated by a hydro extractor, and the mother liquor is treated with the calculated quantity of KCl, [1] there being only 1·2 $CaCl_2$ present to 1 $KClO_3$, the mother liquors cause a very much smaller loss than in the ordinary process. Péchiney's process is specially suited, and was originally invented, for the manufacture of sodium chlorate (cf. infra). It is evidently only possible to work it in the cold season, unless artificial cooling is employed.

The crude chlorate of potash is always purified by recrystallisation ('finished'). For this purpose it is redissolved in a mixture of water and of the mother liquor obtained in the finishing process, which is done in a lead-lined vessel, with the aid of steam, preferably indirect steam. The solution is made at a full boiling heat, sometimes with the addition of very small quantity of sodium carbonate and of sodium sulphide, in order to precipitate any iron and lead present; it is made up to 25°Tw., and, after good settling and straining through canvas, the liquor is run into the coolers. These are made of iron lined with lead (wood lined with lead is not so good); they are either of a deep pattern, with wooden laths placed inside for

the crystals to adhere to, or else they are made quite shallow, but covered over to prevent any too rapid cooling. The crystallisation lasts from 8 to 14 days, according to the season.

The crystals are drained, washed on the drainer, and then again drained in a hydro extractor. This is imperative, since it is required that chlorate of potash should show little or no trace of chlorides; 0·05 p.c. being a maximum sometimes stipulated. So long as there is $PbCl_2$ present, this cannot be very easily effected, but the lead can be removed in dissolving, as stated before. The mother liquors and washings are used over again till they become too impure, when they go back to the boiling-down pans. The crystals are dried on a hollow iron plate, covered with sheet lead, and heated by steam.

Chlorate of potash is either sold as 'crystals' or 'ground.' For the former purpose the crystals, as they come from the drying plates, are sifted through a sieve with eight holes to the linear inch, or less, as the case may be. The powder is best ground while still slightly warm. The mills may be of any description, horizontal, edge runners, rollers; but the chlorate during grinding ought not to come into contact with iron, nor with any organic substance (straw, wood chips, &c), or dangerous explosions may occur. It must be sifted through a revolving sieve, made of miller's gauze, with mechanical brushes. The powder ought to be snow-white, and without any grittiness, like fine flour. The crystals ought to be thin, brilliant transparent plates; excessive drying will make them opaque. Both are usually packed in 1-cwt. kegs, laid out with blue paper.

The loss of the chlorine used to amount to about 38 p.c., with the new processes the losses are about 30 p.c., or at least 25 p.c. The loss of the potassium amounts to 25 p.c.

Magnesia Chlorate of Potash Process.—The great loss of chlorate in the ordinary process has given rise to the process of Muspratt and Eschellmann, where magnesia is substituted for lime (Eng. Pat. 3960, 5183, and 5186 of 1883; and 1900 of 1885). A detailed description of this process has been given by Higgins (J. Soc. Chem. Ind. 1887, 248). The magnesia is obtained by burning Greek magnesite at not too high a temperature; when overburnt it is useless for the absorption of chlorine. The MgO is very finely ground, suspended in water, and exposed to the action of chlorine in the ordinary octagons. The reaction is not so violent as with lime. The temperature of a finished octagon is usually 43°, and it never exceeds 60°. In the finished liquor the proportion of chlorate to chloride is very near to the theoretical, viz. 1 : 5·1 or less; this constitutes an important advantage over the lime process, 7 p.c. less chloride being formed. No pink colour appears with very pure magnesia, but it does when it contains manganese. The strength of this liquor varies from 1·17 to 1·22.

The octagon liquor is now boiled down to 75°–80°Tw., when on cooling about 50 p.c. of the chloride will crystallise out as $MgCl_2,6H_2O$. The mother liquor contains 1 mol. chlorate to 2·8 chloride. Potassium chloride is now added to it in slight excess, and the potassium chlorate crystallised out. The mother liquors being

much less in quantity than with lime, and $KClO_3$ being less soluble in $MgCl_2$ than in $CaCl_2$, the magnesia mother liquors contain much less chlorate than lime liquor (on an average 19 grams down to 10 grams per litre), and the yield of $KClO_3$ rises to 90 p.c. of the total.

The mother liquor is treated with HCl to destroy the chlorate, with due precautions against explosions. The still liquor is now neutralised with MgO; a solution of kieserite ($MgSO_4$) is then run in to decompose the calcium chloride present, and the gypsum, along with iron oxide, is settled out. The liquor is now concentrated in cast-iron pots (wrought iron is acted upon too much); the iron dissolving in the liquor is oxidised to the ferric state, and is precipitated by MgO; the settled liquor is run into barrels, where it sets to a hard mass containing 47 p.c of $MgCl_2$. This magnesium chloride is sold to cotton sizers

This process would, of course, only become general if the magnesium chloride obtained as a by-product could be profitably decomposed for chlorine, as it is not saleable by itself in very large quantities, and could not compete in price with the Stassfurt article. Such utilisation of magnesium chloride for the manufacture of chlorine had been intended by Weldon, who first proposed magnesia for the above purpose, and it is again mentioned in a patent of J. Wilson (5975 of 1884). Twyman (4397 of 1881) proposes dolomite, under the idea that double chloride of potassium and magnesium (carnallite) will crystallise out of the mother liquor after the chlorate (This seems quite hopeless, since the principal question is not that of saving KCl, but $KClO_3$.)

Electrolytic Chlorate of Potash Processes are the most recent. In the preparation of chlorine from potassium chloride solution by the Griesheim process when using magnetite anodes the by-product formed is potassium chlorate, and it crystallises out in the anode cells and is recovered. More direct methods are described under Sodium chlorate.

Uses of chlorate of potash are principally for the manufacture of lucifer matches, for pyrotechnical purposes, for fuses, for some descriptions of gunpowder, and other cases where it is a constituent of explosive materials. It is also largely employed, on account of its oxidising properties, in dyeing and calico printing, in the manufacture of alizarin, &c.

Sodium chlorate. This compound, which formerly was only a chemical curiosity, has become of technical importance, since it was found that it is much more suitable for the preparation of aniline black than potassium chlorate, owing to its greater solubility.

It was at first thought that it could not be prepared from the calcium-chlorate liquor of the ordinary process, because $NaClO_3$ is very soluble, and cannot be separated from $CaCl_2$ by crystallisation, and when a demand for it sprang up, it was made from potassium chlorate by means of hydrofluosilicic acid (*cf.* Lunge's Alkali, 3, 320), and was sold at two or three times the price of the potassium salt.

The process of Bottomley and Molesworth (Pat. 3005 of 1881) consists in treating a hot saturated solution of potassium chlorate with one of bitartrate of soda, and separating the

precipitated potassium bitartrate from the solution of sodium chlorate.

The manufacture of chlorate of soda from calcium chlorate liquor was first carried out by Péchiney, by means of his process of removing most of the calcium chloride from the crude liquor by crystallisation. The purified liquor thus accumulated during the colder part of the year is mixed with a solution of ordinary sodium sulphate, that is saltcake, neutralised by lime before it is used, with continuous agitation, until all the calcium soluble salts have been converted into calcium sulphate, and final additions of either liquor are then made until neither is in excess. The $CaSO_4$, which, under the proper conditions, is crystalline, is then separated from the liquor by filtration and washed in a hydro extractor. The solution of sodium chlorate and sodium chloride is now concentrated by evaporation, during which most of the sodium chloride separates in the solid form and is fished out. The remaining solution on cooling yields crystals of sodium chlorate, which are purified by recrystallisation. The purified sodium chlorate crystals contain no more than 0·16 p.c. NaCl. The mother liquors from the chlorate crystals, and the washings of the sodium chloride, go back into the process, and thus nearly all the chlorate contained in the liquor is obtained.

Chlorate of soda is manufactured by the Muspratt Chlorate Process by means of their magnesium chlorate liquor, freed from nearly half the $MgCl_2$ by evaporation and crystallisation (*cf. supra*). To this liquor sodium carbonate is added, till all the magnesia is precipitated as a basic carbonate (magnesia alba), in order to be used over again in the process. The remaining solution of $NaClO_3$ and NaCl is concentrated by evaporation, with fishing out the NaCl, and after attaining 120°Tw., is allowed to cool down; the sodium chlorate crystallises out, and is purified in the usual manner.

Manufacture of Alkaline Chlorates by Electrolysis. The passing of an electric current through a solution of NaCl or KCl liberates Na or K at the cathode, and Cl at the anode. The Na or K at once decomposes H_2O to form NaOH or KOH and hydrogen gas. If the electrolyte is heated from 45° to 100°, and the caustic alkali is removed promptly from the cathode to the anode, the Cl liberated is absorbed in the caustic alkali produced to form chlorate. There are, however, a number of secondary reactions, both at the anode and the cathode, and the electrolysis of the chloride cannot be carried to completion, because the product, the chlorate, is itself subjected to electrolysis and so destroyed. Theoretically, a current of 1 ampere will produce in 1 hour 0·7627 gram $KClO_3$, or 0·663 gram $NaClO_3$.

Gall and Montlaur, in their Eng. Pat. 4686 of 1887, describe the production of alkaline chlorates by the electrolysis of alkaline chlorides in a trough divided into two parts by a porous diaphragm. The anodes are platinum-iridium sheets containing 10 p.c. of iridium; the cathodes are iron, though it is stated that nickel would be preferable. The electrolyte consists of a 25-p.c. solution of KCl, kept at a temperature of about 80°. The liquor from the cathode compartment containing the alkaline hydrate

there produced, is circulated through the anode compartment and combines with the chlorine liberated. A current density of 50 amperes per square decimeter is used, and a pressure of 4·5 to 5·0 volts is required. In the case of potassium chlorate, the anode liquor is run into crystallising vessels, where the $KClO_3$ crystallises out, and the mother liquor, after resaturation with KCl, is passed back to the cathode compartment. In the case of sodium chlorate the anode liquor has first to be concentrated to crystallise out the NaCl before crystallising out the $NaClO_3$. The crystals obtained require, of course, to be refined by recrystallisation, as in the case of those produced by chemical processes.

Hurter (Eng. Pat. 15396 of 1893) electrolyses KCl in a metal vessel which acts as cathode, and which has on its inner side a coating consisting of a mixture of Portland cement, salt and sand, which, after washing out the salt, yields a porous diaphragm. The anode is a sheet of platinum suspended in the centre of the vessel. Several vessels are superposed and worked in series, being kept apart by insulating rubber rings. A solution of KCl containing a little caustic alkali is run into the top vessel, from which it overflows, through a glass or ebonite pipe, into the cell below. The hydrogen evolved escapes by pipes from the upper part of each compartment.

Blumenburg (Eng. Pat. 9129 of 1894) describes a cell with a porous diaphragm in which the anode compartment is closed and connected by a pipe with the bottom of the cathode compartment, so that the chlorine liberated at the anode passes into the liquor in the cathode compartment, and there combines with the caustic alkali produced, the temperature being maintained at a temperature of about 49°. In the Ger. Pat. 89035, and also in the U.S. Pat. 537179, Blumenburg passes the chlorine gases from the anode compartment into a gas holder, from which they pass to a separate combining vessel, where they are absorbed in the alkaline liquor from the cathode compartment. Chlorate is also formed as a by-product in the Griesheim cell described above, when using the oxide of iron anode.

In 1899 Imhoff made a great advance in the electrolytic production of chlorate by his discovery of the action of small quantities of chromate of potash or soda in the electrolyte (U.S. Pat. 627063 of 1899). The action of the chromate is to form an insoluble film around the cathode, and so to prevent the reduction of hypochlorite and chlorate by the nascent hydrogen evolved in a very marked and important improvement in the current efficiency.

Details of the electrolytic chlorate processes up to 1903 were collected by J. B. C. Kershaw and published as vol. 19 of the Monographien der angewandte Elektrochemie, under the title, Die elektrolytische Chloratindustrie, 1905, p. 122.

Perchlorates of Potassium, Sodium, and Ammonium. That by the electrolysis of chlorates there were formed perchlorates, was first shown in 1816 by Stadion, and in 1847 confirmed by Kolbe. With the aid of such electrolytic methods the above-named per-

chlorates have been manufactured in Mansboe, Sweden, since 1895, in considerable quantities (Carlson, Zeit. für Elektrochemie, 6, 471), and since 1901 in Chedde, France (see Lederlin, D. R. P. 136678). The ammonium salt is used in the manufacture of explosives. Laboratory experiments are described by Foerster (Zeit. fur Elektrochemie, 4, 386) and Winteler (Chem. Zeit. 22, 90); see Kershaw, Elektrolytische Chloratindustrie, p. 67.

Hydrochloric Acid. Commercial hydrochloric acid is a more or less pure solution of hydrogen chloride HCl in water.

Hydrogen chloride is a colourless gas, of sp.gr. 1·2596 (air=1), and molecular weight 36·457. By weight it consists of 2·74 parts of hydrogen and 97·26 parts of chlorine. It can be condensed into a liquid by cold and pressure. Its m p is −111·4°, and b.p. −83·1°, and its critical constants $+51·4° \pm 0·1°$ and $81·55 \pm 0·15$ atmospheres.

The vapour pressures can be expressed between 10° and 51·4° by the formula :

$\log p = 1·152048 + 0·010312(t-10·2)$
$\qquad\qquad - 0·000019989(t-10·2)^2$

and between −24·2° and 10° by the formula :

$\log p = 1·10106 + 0·013277(t+24·2)$
$\qquad\qquad - 0·000039978(t+24·2)^2$

(Cardoso and Germann, J Chem. Phys. 1912, 10, 517; 11, 632).

The heat of formation of a gram-molecule of HCl is 22001 cals.

Hydrogen chloride has a great affinity for water, and is greedily absorbed by it. The solution is the ordinary hydrochloric acid which, when somewhat concentrated, emits fumes of HCl on exposure to the air. The following table by H Deicke shows the maximum solubility of HCl in water at varying temperatures. 1 c.c. dissolves at the temperature $t°$ from an atmosphere of pure HCl at 760 mm. pressure :—

$t°$	Vols HCl at 0° and 760 mm dissolved in 1 vol H_2O	Specific gravity of the saturated solution	Percentage of HCl by weight in the solution
0°C.	525·2	1·2257	45·148
4	494·7	1·2265	44·361
8	480·3	1·2185	43·828
12	471·3	1·2148	43·277
14	462·4	1 2074	42·829
18	451·2	1·2064	42·344
23	435·0	1·2014	41·536

The behaviour of aqueous solutions of HCl under varying conditions of temperature and pressure has been studied by Roscoe and Dittmar (Chem. Soc. Trans. 12, 128). They found that concentrated hydrochloric acid on heating loses both gas and water, but as the proportion of HCl to H_2O is higher in the vapour than in the original liquid, the residual liquid gradually becomes weaker, until a sp.gr. of 1·101 and a percentage of 20·24 HCl is attained at a boiling temperature 110°; the acid in this state distils without change, provided the atmospheric pressure is 760 mm. At a lower pressure the acid distilling unchanged is stronger, at a higher pressure it is weaker. A similar, but not identical

limit is attained when strong acid is exposed to the air at ordinary temperatures.

The following table gives the percentages of HCl in aqueous hydrochloric acid at various specific gravities and at a temperature of 15°:—

hydrochloric acid of commerce was obtained as a by-product of that process; at first the process produced enormously more hydrochloric acid gas than could be sold as hydrochloric acid liquor,

Deg. Twaddell	Spec. gravity	Percentage of HCl	Grams HCl per litre	1 cubic foot weighs lbs.	1 cubic foot contains lbs of HCl
1	1·005	1·12	11·32	62·66	0·70
2	1·010	2·12	21·45	62·97	1·34
3	1·015	3·12	31·67	63·29	1·97
4	1·020	4·11	41·99	63·60	2 61
5	1·025	5·11	52·41	63·91	3·26
6	1·030	6·11	62·93	64·22	3·92
7	1·035	7·10	73·55	64·53	4·58
8	1·040	8·10	84 27	64·84	5·25
9	1·045	9·10	95·09	65·16	5·93
10	1·050	10·09	106·01	65·47	6 61
11	1·055	11·09	117·02	65·48	7·31
12	1·060	12 09	128·14	66·09	8·00
13	1·065	13·08	139·36	66·40	8·69
14	1 070	14 08	150 68	66·71	9 40
15	1·075	15 08	162 10	67·03	10 11
16	1 080	16·07	173·62	67·34	10·83
17 ·	1·085	17·07	185·24	67·65	11 55
18	1·090	18·07	196·96	67 96	12·28
19	1 095	19·07	208 78	68 27	13 02
20	1·100	20·06	220 70	68 59	13 76
21	1 105	21 06	232·68	68·90	14·51
22	1·110	22·06	244 80	69 21	15·27
23	1·115	23·05	257 02	69 52	16·04
24	1 120	24·05	269·34	69 83	16 79
25	1·125	25 05	281·76	70 14	17·57
26	1·130	26·04	294 28	70 46	18·35
27	1·135	27·04	306·90	70 77	19·14
28	1·140	28·04	319 62	71·08	19·93
29	1·145	29·03	332·44	71 39	20·73
30	1·150	30·03	345·36	71·70	21·54
31	1 155	31 03	358·34	72·02	22 35
32	1·160	32·02	371·44	72·33	23 16
33	1·165	33 02	384·64	72·64	23·99
34	1·170	34·02	397·94	72·95	24 82
35	1·175	35·01	411·34	73·26	25 65
36	1·180	36·01	424 84	73·57	26·49
37	1·185	37·01	438·44	73·89	27·34
38	1·190	38·01	452·14	74·20	28·20
39	1·195	39·00	466·00	74 51	29·06
40	1·200	40·00	479·84	74·82	30·00

Lunge and Hurter's Alkali-Maker's Hand-book gives somewhat lower figures; they also give the following table for correcting the hydrometer readings for varying temperatures.

THE MANUFACTURE OF HYDROCHLORIC ACID

In former days small quantities of acid were produced by decomposing common salt with sulphuric acid in cast-iron cylinders, and in order to utilise the more expensive sulphuric acid, an excess of common salt was used. The solid product left in the cylinder consisted of sodium sulphate, mixed with 20-30 p.c. NaCl and was commercially known as cylinder cake. The production of hydrochloric acid from cylinders has, however, practically ceased.

Some time after the establishment of the Leblanc soda process in this country all the

INFLUENCE OF TEMPERATURE ON THE SPECIFIC GRAVITY OF HYDROCHLORIC ACID.

100°	95°	90°	85°	80°	75°	70°	65°	60°	55°	50°	45°	40°	35°	30°	25°	20°	15°	10°	5°	0°
1·121	1·123	1·125	1·127	1·129	1·131	1·133	1·136	1·138	1·140	1·142	1·144	1·147	1·149	1·152	1·154	1·157	1·160	1·163	1·165	1·168
1·110	1·112	1·114	1·116	1·119	1·121	1·123	1·126	1·128	1·130	1·132	1·134	1·137	1·139	1·142	1·145	1·147	1·150	1·153	1·155	1·158
1·099	1·102	1·104	1·106	1·109	1·111	1·113	1·116	1·118	1·120	1·123	1·125	1·127	1·129	1·132	1·134	1·137	1·140	1·143	1·145	1·148
1·088	1·090	1·093	1·095	1·097	1·100	1·102	1·104	1·107	1·109	1·112	1·114	1·117	1·119	1·122	1·125	1·127	1·130	1·133	1·135	1·138
1·078	1·081	1·084	1·086	1·089	1·091	1·094	1·096	1·099	1·101	1·103	1·106	1·108	1·110	1·112	1·115	1·117	1·120	1·123	1·125	1·128
1·070	1·073	1·075	1·078	1·080	1·083	1·085	1·088	1·090	1·093	1·094	1·097	1·099	1·101	1·103	1·105	1·107	1·110	1·113	1·115	1·118
1·061	1·064	1·066	1·069	1·071	1·073	1·076	1·078	1·080	1·082	1·084	1·086	1·088	1·090	1·092	1·095	1·097	1·100	1·103	1·105	1·108
1·053	1·055	1·057	1·059	1·061	1·063	1·065	1·067	1·069	1·071	1·073	1·075	1·077	1·080	1·082	1·085	1·087	1·090	1·093	1·095	1·098
1·045	1·047	1·049	1·051	1·053	1·054	1·056	1·058	1·060	1·062	1·064	1·066	1·068	1·070	1·073	1·075	1·077	1·080	1·083	1·085	1·088
1·037	1·039	1·041	1·043	1·044	1·046	1·048	1·049	1·051	1·053	1·055	1·057	1·059	1·061	1·063	1·066	1·067	1·070	1·073	1·075	1·078
1·025	1·027	1·029	1·031	1·033	1·034	1·036	1·038	1·040	1·042	1·044	1·046	1·048	1·050	1·053	1·055	1·057	1·060	1·063	1·065	1·068
1·013	1·015	1·017	1·019	1·021	1·023	1·025	1·027	1·029	1·031	1·033	1·035	1·038	1·040	1·043	1·045	1·047	1·050	1·053	1·055	1·058
1·001	1·003	1·005	1·007	1·009	1·011	1·014	1·016	1·018	1·020	1·022	1·025	1·027	1·030	1·032	1·035	1·037	1·040	1·043	1·045	1·048
0·991	0·993	0·995	0·997	0·999	1·001	1·003	1·005	1·008	1·010	1·012	1·014	1·017	1·019	1·022	1·024	1·027	1·030	1·033	1·035	1·038
0·981	0·983	0·985	0·987	0·989	0·991	0·993	0·995	0·998	1·000	1·002	1·004	1·007	1·009	1·012	1·014	1·017	1·020	1·023	1·025	1·028
0·971	0·973	0·975	0·977	0·979	0·981	0·983	0·985	0·988	0·990	0·992	0·994	0·997	0·999	1·002	1·004	1·007	1·010	1·013	1·015	1·018

and some of the difficulties encountered in consequence are detailed in the following account.

New sources of hydrochloric acid arose when acetic acid began to be chlorinated by the Badische Anilin und Soda Fabrik in great quantities for the manufacture of monochloracetic acid and artificial indigo, and as one after another organic compound came to be chlorinated. Lastly, since the output of chlorine from the electrolysis of the chlorides of potassium and sodium was not sufficiently readily taken up, processes are now proposed of converting chlorine into hydrochloric acid either with the aid of hydrogen obtained in the decomposition of wood or of the hydrogen obtained at the same time as the electrolytic chlorine.

Hydrochloric Acid obtained in manufacturing Sodium Sulphate (Salt Cake). When Leblanc decomposed salt in order to obtain sodium sulphate he proposed to convert the hydrochloric acid gas evolved into ammonium chloride; but when the Leblanc soda process was introduced into this country that part of his suggestions was not carried out, and the acid gas was regarded as possessing no value, and it was simply allowed to escape into the air. This continued to be the case even after that manufacture had attained a comparatively large extension, but the damage caused to the neighbourhood by the acid gases soon brought about the intervention of local authorities and courts of law, and manufacturers were compelled to pay compensation for the damages they had done. Repeated penalties compelled the alkali manufacturers to seek means for condensing the acid gas. This was first successfully done in 1836 by Gossage's coke towers, but for many years after this there was still considerable damage done by escaping acid gas. The continued disregard by the old alkali manufacturers for the rights of their neighbours led in Belgium, in 1856, to a Parliamentary Commission, and in this country in 1863 to Lord Derby's Alkali Act, and the several subsequent Acts, by means of which British alkali makers were compelled to adopt thoroughly efficient means for condensing their hydrochloric acid, and this has benefited all other manufacturing countries as well.

The reports made by the inspectors under the Alkali Acts form an invaluable record of all the various steps taken for improving the condensation of hydrochloric acid, and have helped to spread a better knowledge of that process and have caused manufacturers to improve it up to the highest standard of efficiency.

The Alkali Acts of 1863 made it incumbent upon those decomposing salt to allow no more than 5 p.c. of the hydrochloric acid to escape into the atmosphere. An additional Act of 1874 prescribed that no more than 0·2 grain of HCl might be present in a cubic foot of the gas escaping from the factory into the air. This corresponds to 0·454 gram HCl per cubic metre, or about three ten-thousandths by volume. The latter clause applies to the chimney gases as well, and not merely to the gases escaping directly from the condensing apparatus. Although these requirements were at first declared by many to be impossible of fulfilment, the actual results proved at once that

they were quite possible, and the escapes registered by the Alkali Inspectors have averaged far below the limits assigned by the Acts. In 1885 only 2·13 p.c. of the total hydrochloric acid was allowed to escape, and the chimney and other gases escaping into the air contained only 0·10 grain HCl per cubic foot. No change has been made in the limit fixed in 1874, and the working of that Act remains satisfactory. Compare the survey of these Acts by the Chief Inspector under these Acts in J. Soc. Chem. Ind. 1892, 120.

Although the various processes and apparatus used for the manufacture of sulphate of soda produce gases differing within wide limits in temperature and concentration of HCl, an efficient condensation, *i.e.* practically complete absorption of the HCl in water to form a liquid acid of 1·15–1·17 sp gr is usually obtained.

The efficiency of the condensation of gaseous HCl in water is dependent on three considerations :

1. Temperature of the gas and of the liquid.

2. Concentration of HCl in the gases to be scrubbed and of the acid liquid to be produced.

3. Time of contact between the gas and the liquid, and the average distance between the gaseous particles and the liquid particles, and also the thickness of the liquid layer, and on its motions internal and as a whole.

On issuing from the sulphate of soda plant the acid gases require cooling. The apparatus used for this purpose depends on the temperature of the gases.

If the gases issue from the pot or pan of a handworked saltcake furnace, the temperature is comparatively low In this case the cooling is usually done in a row or rows of earthenware pipes. The pipes used are often unglazed, but are rendered impervious to moisture and gas by boiling in tar. In some cases the earthenware pipes are substituted by glass pipes of 12 inches diameter, made slightly taper, as shown in Fig. 27. The glass pipes are, of course, more liable to breakages by accident, and also through the effect of violent changes of temperature, than the earthenware pipes, but in sheltered positions they last well.

For the hotter gases issuing from the furnace of an ordinary muffle hand sulphate of soda furnace, or from the cylinders of the Hargreaves process, cast-iron pipes are usually used to cool the gases down to a safe temperature before passing them as before into earthenware or glass pipes. The action of the hydrochloric acid gases on cast iron, when at a temperature well above condensing-point of liquid acid, is very slight.

FIG. 27.

When open furnaces, whether 'hand' or 'mechanical' (such as the Mactear furnace), are used, the acid gases are mixed with the products
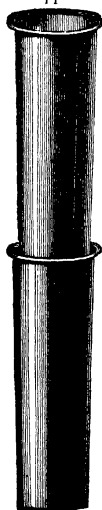
of combustion, and are consequently both much 45°, or even to 25°. The cooling of weak gas is hotter and more dilute. Under these conditions far more important than the cooling of strong gas. extensive series of cast-iron pipes are used for the preliminary cooling before passing the gases into the earthenware pipes for final cooling.

The earthenware pipes used are usually 12-inch or 15-inch diameter socket pipes, the joints being made with a cement of tar and China clay. The cast-iron pipes vary from 12 to 20 inches in diameter, according to the quantity of gas, and the arrangement of the cooling system of pipes; they are socket pipes, the joints being made by ramming into the socket iron filings moistened with ammonium chloride solution.

The arrangement of the cooling pipes depends on the relative positions of the salt-cake furnaces and of the acid condensers and the space available. When the salt-cake furnace is a long distance from the condensers, a single direct line of pipes may be a sufficient means of cooling; where the distance apart is small the necessary amount of cooling surface is obtained by adding extra lengths of pipe that run vertically up and down and that start from a small stone cistern and return to another stone cistern for the purpose of collecting any liquid deposited

Fig. 30.
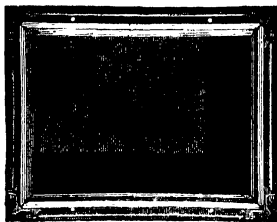
Fig. 28.

The cisterns are usually made in this country of silicious sandstone found in Yorkshire, and known as 'Yorkshire flag.' The cisterns
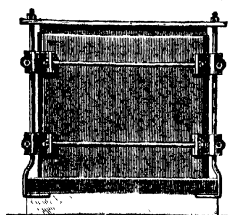
Fig. 29.

are composed of flags 4–6 inches thick, bound together by strong iron ties, and the joints made tight by thick india-rubber cord laid in a groove between the faces of the two stones or

by a mixture of tar and fire clay, as in Fig. 30. By one or more of the above arrangements of pipes and cisterns the acid gases are cooled to
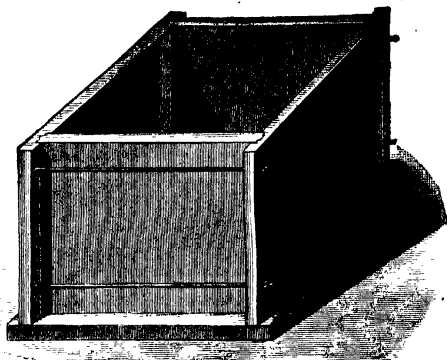
The gases next enter the apparatus where the hydrochloric acid gas is to be converted into a liquid acid of commercial strength, and that in such a manner that practically hardly a trace of acid escapes condensation.

The apparatus almost universally used are tall stone towers, packed with broken coke specially arranged, down which a stream of water is allowed to trickle, and up which the gases are caused to flow (Fig. 31). These towers were invented and patented by Gossage, in 1836.

The coke tower has the merit of simplicity, and, when carefully packed, of efficiency.

The comparative efficiency of various modes of treating liquids with gases has been dealt with in a series of papers by Hurter, who also gives some interesting data on coke-packed towers (J. Soc. Chem. Ind 1885, 639; 1887, 707; and 1893, 227 and 989).

Coke towers are erections of considerable height, varying from about 40 feet to 60 feet. The horizontal sectional area may vary from 25 to 180 square feet. They are provided with a grating a few feet over the bottom, on which
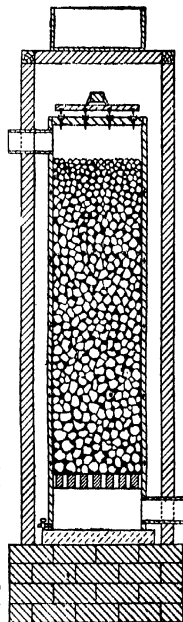
Fig. 31.

rests the coke which forms the 'packing' of the tower. This coke, which must be of as hard a quality as possible (only the best oven-coke is applicable for this purpose), is disposed in such a way that the gas is as much as possible divided in a large number of channels (none of them being so wide that the bulk of the gas can pass up through it), and that the current of gas is constantly changed in direction. For this object long pieces of coke are laid parallel in a row; the next row is made to cross the lower one, and so forth. The size of the pieces is gradually diminished from bottom to top. In order to avoid an excessive quantity of the gas passing up the side of the condenser along the wall, it is usual to place a layer of finer coke round the condenser for a few inches from the wall. By this arrangement there is effected both a great division and constant mixture of the gases, and at the same time a suitable
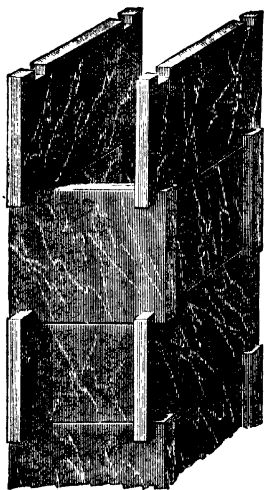
Fig. 32.

spreading of the feeding water over a very large surface. One great advantage coke has over flints or other packings is that, owing to the roughness of its surface and its porousness, it always retains a large store of liquid, which tends to keep the working of the condensers steady under a fluctuating flow of acid gases, and to tide over difficulties occasioned by any unintentional stoppage of the liquor supply. The water (or sometimes weak acid) is fed in at the top by some contrivance assuring a uniform distribution over the whole area of the tower; and in trickling down it keeps the surfaces of the coke moist, and a very large area of contact between the gases and the liquid is thus produced. These towers are so simple to construct and so effective that of recent years there has been a growing tendency in England to do away with all cooling pipes, cisterns, wash towers, &c., and to use a couple of very large stone towers to

do the whole work of cooling and condensation for two or even more salt-cake pots and furnaces. The towers are worked in series, the weak acid from the second or final tower being run down the first tower. In this way both complete absorption of the acid is assured, and the production of a strong liquid acid, i.e. one of over 1·15 sp.gr. To condense the acid from two-hand salt-cake furnaces the two towers may each be 5 feet square and 50 feet high.

No difficulty is now experienced in pumping the weak acid made in the second condenser on to the top of the first condenser, either by stoneware ram pumps, ebonite ram pumps,
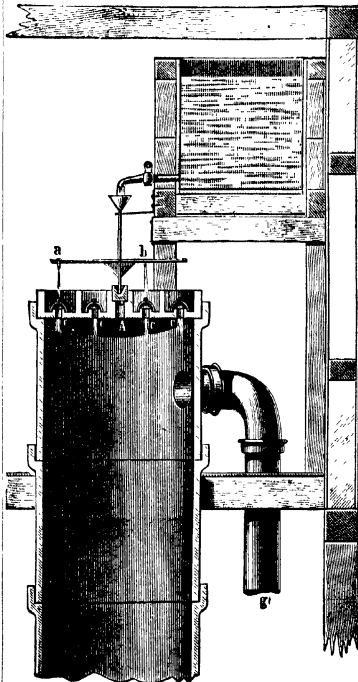
Fig. 33.

stoneware acid eggs, or occasionally even yet by the Hazlehurst membrane pump, patented in 1876. The ascension pipe is usually of stoneware or ebonite, occasionally of lead.

Brick towers are not to be recommended, as it is practically impossible to keep the numerous joints tight against acid oozing out. Columns of stoneware pipes cannot be made of a large area, and, therefore, are not very well adapted to large works, at least if intended for coke towers; but they do very good service at smaller works, or as supplementary to a large condensing plant of stoneware receivers. The material mostly employed for coke towers is acid proof sandstone or, in France, volvic lava, just as

for acid tanks. The system of joining the flags together is the same as shown in Figs. 28 and 29, or else as in Fig. 30, or as shown in Fig 32, in which the flags are kept together by means of grooves worked in the stone, and without the aid of any ironwork, which is always a source of anxiety in acid condensers.

The coke towers are generally placed at a high level, and are, if necessary, put upon pillars, for the purpose of running the acid from them by gravitation either into chlorine stills, or into store cisterns for sale. They must, of course, have a very secure foundation, in the construction of which not merely the great weight of the tower must be considered, but also the probability that there will be now and then leakages of acid which may make the foundation unsafe. This can be avoided by asphalting the ground in such a way that any acid running down cannot penetrate into the soil, and is conveyed to a safe distance Any damage done to the foundation, even if it amounts to much less
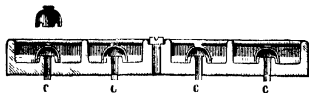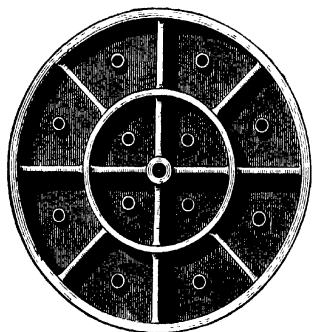
FIG. 34.

than would cause the erection to break down altogether, is extremely injurious, because it will almost unavoidably lead to the tower getting out of level, in which case the liquid will principally descend on the lower side; thus the necessary distribution of the liquid is not attained, and the action of the condenser is most injuriously affected.

It has been already stated that the feeding of the towers with water or with weak acid must take place in such manner as to distribute it equally over the whole surface of the coke. Formerly this was generally done by a distributing wheel (shown in Figs. 33 and 34) worked by the pressure of the feed water itself. Fig. 33 ought to show two jets feeding the outer circle of holes. This causes the stream of water to reach successively every one of the holes on the top of the condenser, and thus secures a uniform distribution without depending upon the top of the tower being at a mathematical level.

Recently most manufacturers have done

away with these acid wheels, and have introduced troughs provided with a number of overflows all at the same level, feeding the same number of 'lutes.' This arrangement is indicated on Fig. 31. This figure represents a tower built as Fig. 32, the cross-hatched outer portion representing the timber framework to support the feeding cistern.

Another form of apparatus for dissolving the hydrochloric acid gas is the Lunge Rohrmann plate tower, shown in Figs. 35, 36, and 37.
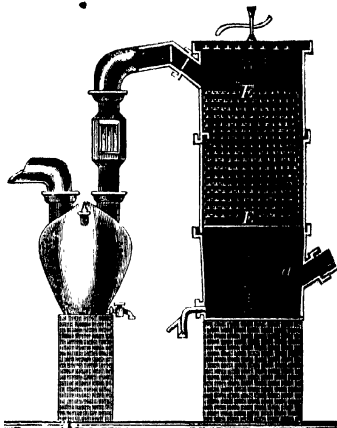
FIG. 35.

It consists of an earthenware tower packed with a series of perforated plates E, E, the perforations being made to alternate in successive plates, so that each hole corresponds to a solid place in the plates just above and below. Figs 36 and 37 show one of the plates in detail. As is to be expected, the evidence for and against the improved packings for the condensing towers is very conflicting, and as the
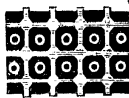
FIG. 36.   FIG. 37.

cost of them is naturally higher, the coke-packed tower has fully maintained its position.

In France and Germany a somewhat different system of cooling and condensation is in general use. The earthenware and glass pipes mentioned above as being used almost exclusively in this country for the cooling of the gases are more or less completely substituted by a series of earthenware Woulffe's bottles, known technically as bombonnes or touries (see Fig. 38). The figure is drawn too small to show that the vessel on the right is about 1 inch higher than the vessel on the left; the liquids travel down hill from right to left, and consequently the gases are made to travel from left to right. The size of the bombonnes varies from 40 to 100

gallons. They are arranged in sets of 40 up to 100, as shown in Fig. 39, and, in spite of the relatively high temperature in the leading
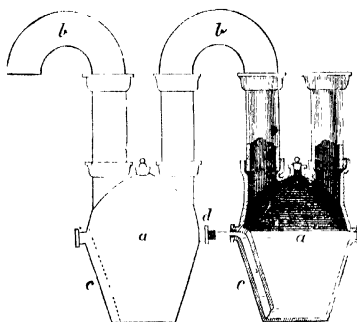
FIG. 38

bombonne, eventually gives a liquid acid of 1·15-1·18 sp.gr. They are made of the best stoneware, which is able to stand somewhat violent changes of temperature. After leaving the bombonnes, the acid gases are finally scrubbed with water in a coke-packed tower, similar in design but usually much smaller than those used in this country. The weak liquid acid produced in this tower supplies the stream of weak acid required by the bombonnes. The figure does not show the means of running off the strong acid from the lowest bombonnes in the series, nor the cisterns, &c., for receiving the acid.

In the condensation of hydrochloric acid gas in water with the apparatus at present used and described above, there is little reason for difficulty in avoiding losses of HCl through incomplete absorption. The difficulty more commonly experienced is to combine the complete absorption enforced by law with a high-strength liquid acid.

The impurities found in commercial hydrochloric acid made by the above processes are, chiefly, sulphuric acid, ferric chloride, arsenic trichloride, and either free chlorine or sulphurous acid.

Sulphuric acid is the largest impurity. The hydrochloric acid condensed from the pan or pot gas is always much purer than that from the roaster gas. The quantity of *sulphuric acid* in the gases from the salt-cake furnace sometimes amounts to 2 p.c. and upwards; it is very troublesome in the Weldon, and fatal in the Deacon, chlorine process, and in some other
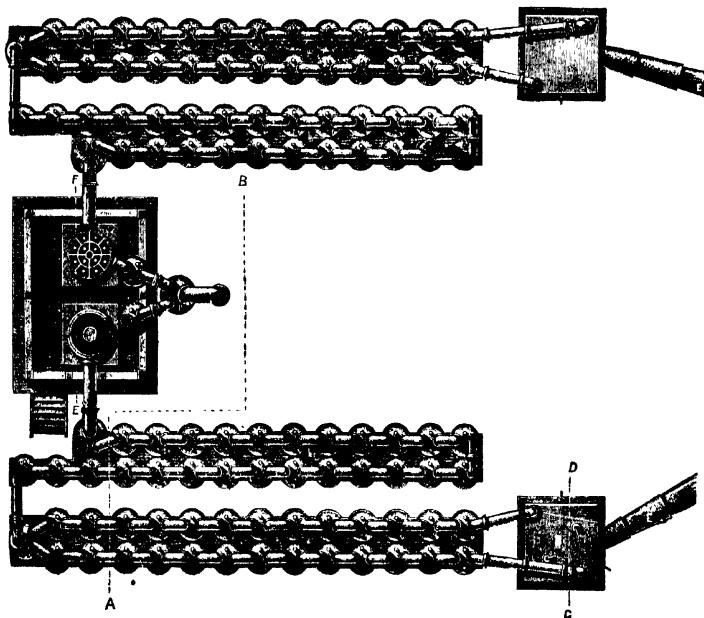
FIG 39

applications of hydrochloric acid. The sulphuric acid in the salt-cake furnace gases can be removed to a large extent by a small condenser or dry scrubber before condensation. A large number of suggestions have been made for the purification of the salt-cake furnace.

gases, so as to render them suitable for the Deacon process, but the only one of these processes to achieve practical success is the Hasenclever process (Eng. Pat. 3393 of 1883). (*See* at end of Deacon Chlorine Process.)

Arsenic gets into the hydrochloric acid through the sulphuric acid employed in its manufacture; the arsenic is thereby converted into AsCl₃, and passes as such into the condensing apparatus. Many plans have been proposed for its removal—most frequently a treatment with sulphuretted hydrogen or with sulphides. Bettendorf (Dingl. poly. J 194, 253) precipitates the arsenic from concentrated hydrochloric acid by stannous chloride, and then distils the decanted acid. Duflos dilutes the acid to sp.gr. 1 13, and digests it with strips of sheet copper at 30°C. for 24 hours, and repeats this treatment with freshly scoured copper. This removes all the arsenic and the free chlorine, and reduces the ferric chloride to ferrous chloride, which remains behind on distillation. Beckurts (Fischer's Jahresb 1884, 348) distils hydrochloric acid with ferrous chloride and removes the first 30 p c. containing all the arsenic.

Selenium is sometimes found in such quantities in hydrochloric acid as to be troublesome in its application (Davis, J Soc Chem. Ind. 1883, 157).

Hydrochloric Acid from other Sources than the Leblanc Process Attempts have been made to produce hydrochloric acid from many sources, notably from the residual liquors of the ammonia-soda process. A number of suggestions have been made for the direct production of HCl : 1st, from CaCl₂ ; 2nd, from MgCl₂ ; 3rd, from NH₄Cl. In this connection compare the references given for the production of chlorine from these bodies earlier in the article As far as is known, none of the processes is used. Mond (1883) heats the ammonium chloride with so much sulphuric acid that the acid sulphate is formed and all HCl is expelled The acid sulphate is converted by means of ammoniacal vapours into the neutral salt of commerce. O. N. Witt (1886) expels the HCl from NH₄Cl by means of syrupy phosphoric acid, which forms ammonium phosphate On heating this at a higher temperature, the ammonia is driven out as well, and the phosphoric acid is regenerated. Jurisch (Dingl. poly. J. 267, 431) has shown that this process is not practicable, because there is no material known which resists the fusing phosphoric acid, and only 63 to 86 p.c. of the NH₃ is recovered. Mond passes the vapour of ammonium chloride over nickel oxide, heated to at least 350°, which absorbs the HCl and allows the NH₃ to pass on. After a certain time the process is changed by raising the temperature to 500° or 600° and decomposing the nickel chloride by steam, when HCl is driven off and NiO regenerated. (Several patents taken out in 1886.)

During recent years, when the chlorination of organic compounds has grown by vast strides, the hydrochloric acid gas produced when a hydrogen atom is substituted by a chlorine atom, has had to be collected and utilised. These reactions are referred to in a previous page when describing the uses of chlorine. The hydrochloric acid gas is evolved almost pure, is easily condensed, and yields an acid quite free from the usual impurities.

Hydrochloric acid has also been produced by passing chlorine over wood at a temperature of 150°-350°, whereby charcoal is also formed (Bosnian Electricity Works at Jacie, D. R. P. 158086).

Lastly, hydrochloric acid has been prepared by processes inverting the practices of the last hundred years, namely, it has been prepared from its elements as a direct and definite process without the formation of by-products, or for any other reasons than its own preparation and the utilisation of the two elements formed by the electrolysis of potassium and sodium chlorides. The gases are mixed and passed over charcoal (D R. P. 114219), or they are burnt together at jets (Soc. Italiana di Elettrochimica ; J. Soc. Chem Ind. 1915, 1142), or they are combined together by Roberts' patent (Electrochemical and Metallurgical Industry, 1910, 704), and by this last process the acid has been manufactured in Niagara since 1914.

The *conveyance* of hydrochloric acid mostly takes place in glass carboys of 10 or 12 gallons capacity with basket or wire hampers, sometimes in earthenware carboys of the same size, and recently hard white vitrefied earthenware jars have become available. At a large French works, some years ago, tank waggons were used, carrying iron cylinders lined with ebonite.

Tank waggons have of late years come into general use, especially on the Continent. They consist of a waggon platform, carrying a number of stoneware jars of about 1 ton capacity each jar. Fig. 40 shows such a waggon carrying 12
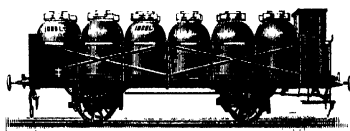
Fɪɢ. 40.

jars, each of which holds 1 ton of acid. Specially prepared wooden tanks are also used occasionally.

The *applications* of hydrochloric acid solution are, first and foremost, for producing chlorine by the Weldon process ; for the cleaning of thin sheet iron when the same is to be coated with zinc, tin, or lead ; for extracting the phosphates from bones and from bone char—for which purposes it must be quite free from sulphuric acid ; for preparing zinc chloride, and zinc ammonium chloride from the residual 'flux skimmings' of galvanising works ; for souring goods during the process of bleaching ; for neutralising the alkaline melts in the manufacture of alizarin, resorcin, &c. ; for the manufacture of aniline hydrochloride, stannous chloride, ferric chloride ; for the preparation of pure carbonic acid from limestone ; in dyeing and tissue printing ; and in the manufacture of many coal tar colours and intermediates, &c.

H. B.

ω-**CHLOROACETOPHENONE** *v.* Kᴇᴛᴏɴᴇꜱ.
CHLOROBENZALDEHYDE *v.* Bᴇɴᴢᴀʟᴅᴇ-
HYDE.

CHLOROBENZENE v. PHENYL.

δ-CHLOROBENZENEDISULPHONIC ACID $C_6H_5Cl(SO_3)_2H_2$. Formed by heating at 300° chlorobenzene with five times its volume of fuming sulphuric acid containing 20 p.c. of sulphur trioxide. Forms barium, potassium and ammonium salts, a dichloride, m.p. 105·5°–106° and a diamide, m.p. 223°–224°. The dichloride heated under pressure at 200°–210° with phosphorus pentachloride yields δ-trichlorobenzene (Olivier, Rec. trav. chim. 1918, 37, 307).

p-**CHLOROBENZENE DIAZOCYANIDES** v. DIAZO- COMPOUNDS.

CHLOROBROM. Trade name for a mixture of equal parts of potassium bromide and chloral formamide dissolved in water.

CHLOROFORM, *Trichloromethane* $CHCl_3$

Chloroform was discovered by Liebig in 1831 (Pogg. Ann. 23, 242), and independently, about the same time, by Soubeiran (Ann. Chim. Phys. [2] 48, 131). Its actual composition was first determined by Dumas (Ann. Chim. Phys. [2] 56, 115) to whom is also due the name by which it is now known. Chloroform is largely employed as an anaesthetic and is an important solvent, finding technical application in the manufacture of fats, rubber, resins, alkaloids, &c. It is also a useful antiseptic.

Formation.—1. By the action of alkalis on chloral (Liebig, Pogg. Ann. 23, 442 ; Annalen, 1, 199 ; 162, 161)

$$CCl_3CHO + NaOH = CHCl_3 + HCOONa$$
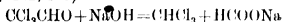
2. By the action of water, ammonia, or alkalis on trichloracetic acid (Dumas, Annalen, 32, 101 ; Beckurts and Otto, Ber. 14, 589)

$$CCl_3COOH + H \cdot OH = CHCl_3 + CO_2 + H_2O$$
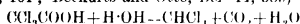
3. By the action of bleaching powder (chlorine) on ethyl alcohol or acetone. In the case of alcohol the reaction has been represented by the following equations :

(a) $CH_3CH_2OH + CaOCl_2$
$$= CH_3CHO + H_2O + CaCl_2$$

(b) $2CH_3CHO + 3CaOCl_2$
$$= 2CCl_3CHO + 3Ca(OH)_2$$

(c) $2CCl_3CHO + Ca(OH)_2$
$$= 2CHCl_3 + (H\,COO)_2Ca$$
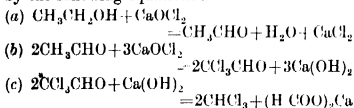
According to Dott (J. Soc. Chem. Ind. 27, 271), however, the reaction is best indicated by the equation

$3C_2H_5OH + 8CaOCl_2$
$$= 2CHCl_3 + 3CaCO_3 + CO_2 + H_2O + 5CaCl_2$$

no appreciable amount of calcium formate being found in the products of reaction.
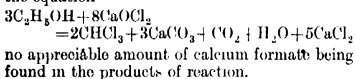
According to Feyer (Zeitsch. Elektrochem. 1919, 25, 115), the formation of chloroform from alcohol occurs in three stages : first, an oxidation of the alcohol to aldehyde ; secondly, a formation of hypochlorite ; and thirdly, an interaction between the aldehyde and the hypochlorite :

(i) $CH_3 \cdot CH_2 \cdot OH + HOCl$
$$= CH_3 \cdot CHO + H_2O + HCl ;$$

(ii) $OH' + Cl_2 = H' + Cl' + ClO' ;$

(iii) $CH_3 \cdot CHO + 3HOCl$
$$= CHCl_3 + HCO_2H + 2H_2O ;$$

(iv) $H \cdot CO_2H + HOCl = CO_2 + H_2O + HCl.$
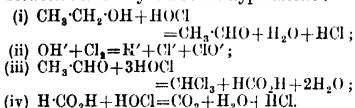
Equation (i) is partly replaced by the reaction *

$$CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CHO + H_2O$$
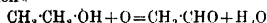
In the case of acetone the reaction may be expressed thus (Orndoff and Jessel, Amer. Chem. J. 10, 363) :

$2CO(CH_3)_2 + 6CaOCl_2$
$$= 2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + (CH_3COO)_2Ca$$

Dott (*loc. cit.*), however, prefers the equation

$2CO(CH_3)_2 + 8CaOCl_2$
$$= 2CHCl_3 + (CH_3COO)_2Ca + 2Ca(OH)_2$$
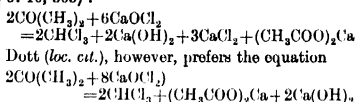
which agrees better with the results of experiment. According to Ukita (J. Chem. Ind. Tokyo, 1918, 21, 219) better yields are obtained by passing chlorine into ethyl alcohol until a liquid of $D = 1·299$ is obtained. This is then added to a solution of bleaching powder and lime and distilled.

Chloroform is also produced from acetic acid (Liebig), acetophenone (Orndoff and Jessel, *loc. cit.*), acetaldehyde turpentine, and terpenes (Chautard, Jahresb. 1851, 501) by the action of bleaching powder or chlorine. ¶F. also Brit. Pat. 1.6094, (1917.)

4 By reactions similar to the foregoing chloroform is also produced by the electrolysis of the chlorides of alkali or alkali earths in presence of alcohol, acetone, &c. (Ber. 1884, 17, Ref. 624 ; *see also* Waser (Chem. Zentr. 1910, I, 1122), Feyer, Zeitsch. Elektrochem. 1919, 25, 115)

5. By the reduction of carbon tetrachloride (Geuther, Annalen, 107, 212 ; *v. also* Chem. Rev. 1896, 88 ; U.S. Pat. 753325 (1904) and Eng. Pat. 13733 (1901)).

6. By the action of chlorine in sunlight on methyl chloride (Regnault, Annalen, 33, 328).

7 From iodoform by the action of phosphorus pentachloride (Gautier, Bull. Soc. Chim. [2] 13, 127).

Manufacture.—Chloroform was originally almost wholly manufactured from ethyl alcohol or methylated spirit Purification of chloroform prepared from the latter presents rather more difficulty, but when properly carried out pure chloroform is obtained.

Of late years chloroform has been made for the most part from acetone, and although for some time a prejudice existed against the employment of chloroform made from this source for anaesthetic purposes, it is now recognised that the product when properly prepared is in every respect equal to that obtained from alcohol.

Chloroform has been manufactured successfully in America for some years past from carbon tetrachloride by reduction with nascent hydrogen. This is most efficiently brought about by mechanically agitating a mixture of the tetrachloride and finely divided iron in water, a trace of acid being added to initiate the reaction (Smith, U.S. Pat. 753325 (1904) ; *see also* U.S. Pat. 1101025, 1914).

Attempts have also been made to manufacture chloroform by chlorination of the ' natural gas ' (methane) produced in enormous quantities in the United States, but so far these attempts have not met with any measure of success.

Electrolytic processes for the production of chloroform from alcohol and acetone have formed the subject of a number of patents, but the commercial results do not seem to have been so successful as the original experimental work promised, and very little chloroform has been made by this means (Schering, **D. R. P.**

29771 (1884), *v. also* Zambelliti, L'Ettricita, 1899, 8, 664 ; Teeple, J. Amer. Chem. Soc. 26, 536 ; and Wäser (Chem. Zentr. 1910, I, 1122).

Manufacture of Chloroform from Acetone and Bleaching-powder.—This is the process most generally employed. The method differs in minor details with the various manufacturers, but the following may be taken as representa-

tive. The reaction is carried out in a cast-iron still of about 800 gallons capacity, which is provided with stirring gear, steam and cooling coils, and is connected with a condenser. Three hundred gallons of water are run into the still, and 800 lbs. of bleaching powder are added through a manhole, which is then securely bolted down. During addition of the bleaching
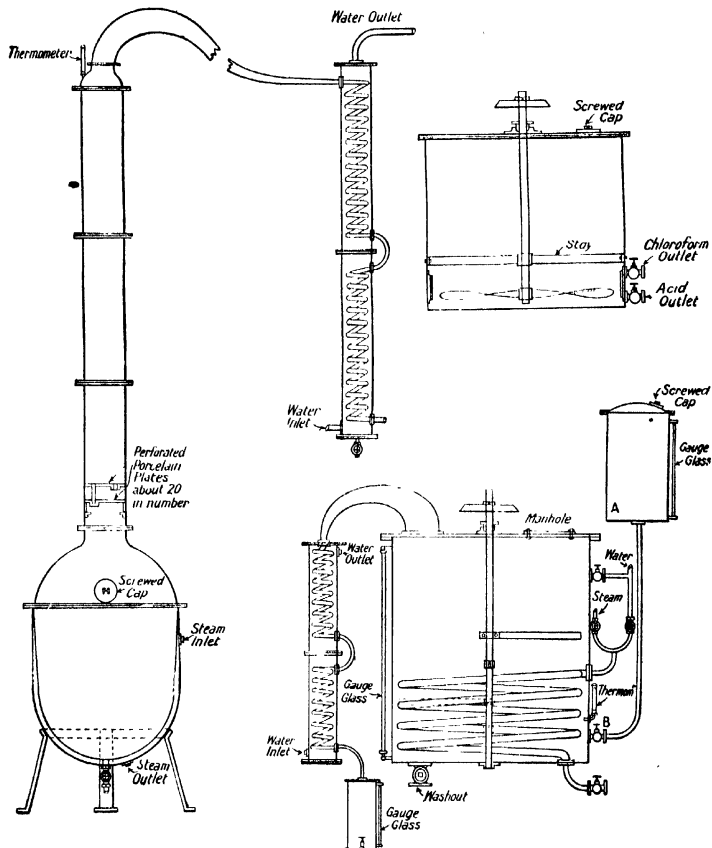
powder the mixture is very thoroughly stirred. (In some processes the mixing is carried out in a separate vessel, and the suspension is strained from the larger unbroken lumps of bleaching powder before being allowed to run into the still.) The container (A in the diagram shown) is charged with 70 lbs. of acetone, which is then slowly run into the bottom of the still by means of the valve B. The introduction of the acetone is accompanied by a rise of temperature which is not allowed to exceed 110°F., cooling being

effected if necessary by stopping the flow of acetone and circulating cold water through the cooling coil in the still. When all the acetone has been introduced the contents of the still are raised to 134°F. At this temperature chloroform begins to distil over. The temperature is then very gradually raised to 150°F., so as to keep the chloroform steadily distilling. Towards the end of the reaction the mixture is stirred and the temperature raised until no more chloroform distils over.

The crude chloroform obtained is separated and purified first by agitation with concentrated sulphuric acid. This operation is carried out in the vessel shown in the diagram ; 1500 lbs. of crude chloroform are introduced into the vessel and thoroughly stirred by means of the agitating gear shown, with 600 lbs. of sulphuric acid. The stirring is continued until a sample of the chloroform, when thoroughly shaken with pure concentrated sulphuric acid, does not impart the slightest colour to the latter. The time required for complete purification is usually about 3 hours. The chloroform is next separated from the sulphuric acid and finally distilled over lime.

The yield obtained from the above quantities averaged from over two thousand batches was 124 lbs., the highest yield in any one case being 131 lbs. Variation in yield is attributed to the varying composition of the bleaching powder, though doubtless other factors influence the result. Bleaching powder containing less than 33 p.c. of available chlorine gives unsatisfactory results, while samples containing more than 35 p.c. of chlorine are also often unsatisfactory. The best results appear to be obtained with bleaching powder containing about 34 p.c. of available chlorine.

Manufacture of Chloroform from Alcohol.— This is carried out in the same plant as that used for the manufacture of chloroform from acetone. A mixture of alcohol (150 lbs.) and water (3000 lbs.) is introduced into the still, bleaching powder (750 lbs.) added, and the contents of the still gently heated by means of the steam coil. Chloroform begins to distil over at a temperature of about 140°–145°F. Further heating is then discontinued, the chloroform distilling off by reason of the heat generated during the reaction. When the distillation begins to slacken the heating is resumed until at a temperature of 155°F. the distillate consists of a mixture of alcohol and water. This mixture, which contains rather more than half the original alcohol, is used in making up the next batch, sufficient fresh alcohol being added to make up the required 150 lbs. The yield of crude chloroform from each working is about 75 lbs. Purification is effected as described above.

Chloroform has also been manufactured by special processes for the purpose of producing directly chloroform sufficiently pure for anaesthetic purposes. Of these the most important are the following :—

1. *Chloroform from Chloral.*—It was found by Liebig, the discoverer of both compounds, that chloroform could be obtained from chloral by distillation with alkalis, and subsequent washing and drying, and this process has been utilised for the manufacture of chloroform. Upon the same reactions has been based a patent (Liebreich, Eng. Pat. 15930, D. R. P. 176063, 1904), whereby a dry mixture of chloral hydrate and alkali can be prepared and compressed, from this product chloroform may be prepared by treatment with water. Chloroform obtained from chloral is of a high degree of purity. Like all other brands of chloroform it must, however, be preserved by the addition of a small amount of alcohol.

2. *Chloroform Pictet.*—This product is ob-

tained by fractionally crystallising commercial chloroform. The crude chloroform is cooled to −80°, and the solid impurities are filtered off. The filtrate is then cooled to −82°, and the liquid portion is drained off. The crystallised chloroform is then distilled at a very low temperature, and the middle fraction amounting to about 80 p.c. is collected as chemically pure chloroform (Pictet, Compt. rend. 114, 1245 ; French Pat. 215911, 1891 ; U.S. Pat. 489592, 1893). It was originally claimed that the ' pure ' chloroform obtained by this means was stable in the presence of light, and from this Schact & Bilz (J. Soc. Chem. Ind. 1893, 12, 543) deduced that it contained a small amount of alcohol which was subsequently shown to be the case.

3. *Chloroform Anschutz* (' Salicylid chloroform ').—Anschutz (Annalen, 273, [1] 94) observed that chloroform combined to form well crystalline compounds with the lactide condensation products obtained from o-phenol carbonic acids. These compounds break up on gentle heating, giving pure chloroform. The compound usually employed in the process is tetrasalicylide $\left(C_6H_4 \diagdown \begin{smallmatrix} CO \\ O \end{smallmatrix} \right)_4$ m.p. 261°–262°, obtained by the action of phosphoryl chloride on salicylic acid. This combines with 3 molecules of chloroform which are given up on warming. The recovered salicylide can be employed again. The product obtained by this process has been extensively used in Russia.

Properties.—Chloroform is a heavy colourless liquid having a sweet taste and a pleasant ethereal odour. It is not inflammable, but when diluted with alcohol may be made to burn and gives a smoky greenish flame. It is very slightly soluble in water (1 part in 200), but miscible with most organic solvents.

According to the most accurate determinations pure chloroform has sp.gr. 1·52637 at 0°/4° (Thorpe, Trans. Chem. Soc. 37, 196), 1·52657 (Timmermans, Bull. Soc. belg. chim. 24, 244), or 1·4989 at 15°/4° (Baskerville and Hamor, J. Ind. and Engin. Chem. 1912, 278). According to the same authors the boiling-point is 61·2° (*see also* Wade and Finnemore, Trans. Chem. Soc., 1904, 85, 946). Chloroform melts at −83° (Pictet). Its critical temperature is 262·9°, and critical pressure 53·8 atmos. (Kuenen & Robson).

Reactions and detection of Chloroform.—The most important reaction of chloroform is the formation of an isocyanide from any primary amine when the latter is heated in presence of chloroform and alcoholic potassium hydroxide solution

$$CHCl_3 + R \cdot NH_2 + 3KOH = R \cdot NC + 3KCl + 3H_2O$$
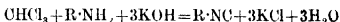
In practice aniline is usually employed as the reacting amine and the characteristic odour of phenylisocyanide is readily recognised. In this way one part of chloroform in 5000–6000 parts of alcohol can be detected. The reaction is also given, however, by bromoform, iodoform, chloral, trichloracetic acid, &c. ; but not by ethylidene chloride. Chloroform readily reduces Fehling's solution and the reaction has been used as an indirect method of estimation.

A mixture of chloroform vapour and hydrogen when passed through a red hot tube yields-

hydrochloric acid. This reaction also may be employed for the detection and estimation of chloroform in blood or other (non-chlorinated) liquids (Allen, Comm. Org. Anlysis, vol. i. p. 275). *a* or *β* naphthol dissolved in concentrated potassium hydroxide solution when heated with a little chloroform give a blue colour which gradually becomes green and finally brown in contact with air.

Anæsthetic Chloroform.—The use of chloroform as an anæsthetic was first advocated by Simpson in 1848 (Edin. Monthly J. Med. Sc. 8, 415), and it is now used in very large quantities for this purpose alone. Great care is necessary in its production for this purpose, since the presence of small amounts of impurities have a deleterious and often dangerous influence, and many cases of death under chloroform have been attributed to the employment of impure anæsthetic. As the result of a considerable amount of investigation, it has now been shown fairly conclusively that pure chloroform under the influence of light, air, and moisture decomposes, more or less rapidly according to the conditions prevailing, and that the products of decomposition are carbony' chloride and hydrochloric acid, a reaction which may be represented thus:

$$CHCl_3 + H_2O + O_2 = COCl_2 + HCl + H_2O_2$$
$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O$$
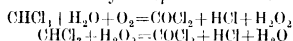
It was very early noticed that the tendency of chloroform to decompose was more marked with samples which showed a high specific gravity (1·497 to 1·50) than with those of lower density, and the greater stability of the latter was attributed to the presence in them of small amounts of alcohol. It had earlier been suggested by Squibb (Amer. Med. Monthly, July, 1857), that the best means of preserving chloroform was the addition of a small amount of alcohol. This practice has since then been recognised as sound in principle and the addition of alcohol in amounts varying from 0·6 to 1·0 p.c. by volume is allowed by most of the pharmacopœias. The British Pharmacopœia (1914) does not specify the amount of alcohol permissible, but defines the density at 1·483 to 1·487.

Considerable diversity of opinion has been expressed with regard to the *rôle* played by alcohol in preventing the decomposition of chloroform, but it now appears to be fairly well established that it acts by reason of its property as a reducing agent, oxidation of alcohol taking place in preference to that of chloroform. At the same time the products of oxidation appear to exert a retarding action which eventually reaches a maximum. When chloroform is preserved with alcohol the decomposition of the chloroform is entirely prevented until all the alcohol is oxidised, when decomposition of the chloroform immediately commences. When properly stored and packed so that the action of light and air is reduced to a minimum, chloroform containing from 0·6 to 1 p.c. by volume of alcohol will keep for years (Schact and Bilz, Pharm. J. 1893, 1005). The theory of the action of alcohol outlined above is due to Baskerville and Hamor (J. Ind. and Chem. Eng. 1912, 368, &c.), whose admirable series of papers form the most complete and recent account of the subject of this article. Their theory is supported by the fact that a large

number of organic substances soluble in chloroform will inhibit the decomposition of the latter by light and air, and that all such compounds are reducing substances and act solely on account of their capacity for oxidation. That such compounds are not used in practice is merely on account of the special suitability of alcohol for the purpose.

The various pharmacopœias also insist on certain tests for the absence of impurities, other than alcohol, which might possibly be present in chloroform through careless manufacture or storage. The details of the tests vary in different countries, but may be generally indicated as follows :—

(1) *The odour test.*—This is usually carried out by evaporating a quantity of chloroform (10–50 c.c.) to small bulk, and then allowing the residue to evaporate on a piece of filter paper. At no stage of the evaporation should there be any appreciable foreign odour, *e.g.* of fusel oil, higher alcohols, or chlorinated derivatives of alcohol or acetone.

(2) *Residue.*—There should be no weighable residue after evaporation of 50 to 100 c.c. of chloroform.

(3) *Sulphuric acid test.*—This consists in shaking chloroform (usually 20 c.c.) with pure concentrated sulphuric acid (usually 15 c.c.) for a short time and then allowing the mixture to stand. The two layers are required to remain colourless or practically so over a period of time which varies with the different pharmacopœias. The object of the test is to detect the presence of organic impurities which should have been removed in the process of manufacture.

A more delicate variation of this test has been suggested by Langgaard (Therap. Monatsh. May, 1902). Concentrated sulphuric acid and chloroform are mixed in the proportions required by the German Pharmacopœia and then four or five drops of formalin (40 p.c. solution) added and the mixture well shaken. No coloration should develop on standing. The German Pharmacopœia requires the solution to remain colourless for forty-eight hours. According to Budde (Veröffentlichungen aus dem Gebiete des Militar-Sanitatswesens, 1913, 6, 113), however, the sensitiveness of the reaction increases with the amount of alcohol present.

(4) *Acidity.*—Water shaken with chloroform and separated should remain neutral to litmus.

(5) *Chlorine.*—The aqueous layer after shaking chloroform with water should give no reaction when shaken with a 10 p.c. solution of cadmium iodide and a few drops of starch solution.

(6) *Hydrochloric acid.*—The aqueous layer obtained as above should not give more than a very slight opalescence with a solution of silver nitrate. (*Cf.* Analyst, 1919, 407.)

(7) *Decomposition products.*—Two c.c. of the sulphuric acid solution obtained as in test (3) when diluted with 5 c.c. of water should remain nearly colourless and have no unpleasant odour. When further diluted with 10 c.c. of water the solution should remain colourless and on addition of a little silver nitrate should not give more than a slightly diminished transparency.

For the last three tests Budde (*loc. cit.*) proposes to substitute one, namely, a reaction with benzidine, which it is claimed is simpler and at the same time more sensitive. A little

pure benzidine is dissolved in about 10 c.c. of chloroform. The solution should remain perfectly bright when kept in the dark, out of contact with air for 24 hours. In the presence of chlorinated products or of carbonyl chloride an opalescence or flocculent precipitate is produced. If chloral is present, a faint red coloration develops at first and changes to bluish-red after a time

Other possible Constituents of Anæsthetic Chloroform.

Ethyl chloride.—Chloroform manufactured from alcohol was at one time considered, for anæsthetic purposes, superior to that obtained from acetone. Wade and Finnemore (1904, 85, 938) showed that chloroform prepared from alcohol contained a small quantity (approx. 0·05 p.c.) of ethyl chloride, and to this they attributed its superior qualities. According to them pure chloroform prepared from acetone, and to which a small proportion of ethyl chloride was added, was alone clinically equal to that obtained from alcohol. Baskerville and Hamor (*loc. cit.* p. 574), however, state that American anæsthetists have found chloroform from acetone when properly purified to be fully as reliable as chloroform from alcohol They therefore look upon ethyl chloride as an impurity of anæsthetic chloroform which although perhaps not objectionable, has no special value. Since the boiling-point of chloroform is lowered to the extent of about 2° by the presence of 0 1 p c. of ethyl chloride (Wade & Finnemore, *loc. cit.*) its presence is easily detected by fractionation.

Acetaldehyde.—For the detection of this impurity in chloroform Baskerville and Hamor suggest the following : 10 c c of chloroform are shaken with 5 drops of Nessler's solution U.S.P. and allowed to stand for five minutes Anæsthetic chloroform should show no precipitate or colouration under these conditions.

For the detection of acetaldehyde chloroform is in practice often tested by allowing to stand over solid KOH. For this purpose the KOH should contain at least 80 p.c. KOH and be free from water, otherwise oxidation of alcohol may take place and a positive reaction be obtained.

Acetone.—Anæsthetic chloroform should give a negative result when tested as follows. To 10 c.c. of chloroform are added 5 drops of 0·5 p.c. solution of sodium nitroprusside and 2 c.c. of ammonia (D=0·925) and the mixture allowed to stand for five minutes in the cold. If acetone is present to the extent of 0·2 p.c. an amethyst colour is produced. By saturating the mixture with ammonium sulphate the colour is produced in the presence of 0·1 p.c. of acetone.

Carbonyl chloride, which is only likely to be present in badly preserved or stored anæsthetic chloroform, may often be detected by its nauseous odour. The following test is also quite satisfactory. To 15 c.c. of chloroform in a dry glass-stoppered cylinder of 25 c.c. capacity is added sufficient clear solution of barium hydroxide (0·5 p.c.) to completely fill the tube, which is then kept in the dark for 3 hours. In the presence of carbonyl chloride a film of barium carbonate is produced at the junction of the liquids.

Carbonyl chloride is also readily detected by the benzidine test (Budde, *loc. cit.*), which gives a positive reaction with one part in twenty thousand (1 : 20,000).

The impurities of commercial chloroform may include chloral alcoholate and similar chloral compounds. These may be estimated by treating the chloroform with N/10 alkali and titrating the excess. Pure chloroform is not affected by alkali of this strength. Aldehydic and similar compounds are detected by means of Nessler's reagent, which gives with impure chloroform a red-brown deposit readily changing to greenish black. Pure chloroform gives no such reaction (Enz. Apoth. Zeit. 1913, 28, 672 ; Analyst. 1913, 497).

Chloroform is comparatively unstable under the influence of ultra-violet radiation (Kailan, Monatsh. 1917, 38, 537).

Detection and Estimation of Alcohol in Chloroform.—For the detection of alcohol in chloroform the iodoform reaction provides a very delicate test which, however, is not specific. It is best carried out by shaking the chloroform with sulphuric acid, separating and diluting the sulphuric acid layer This is then distilled and the reaction carried out on the first portions of the distillate. To 10 c c of the distillate 6 drops of a 10 p c. solution of potassium hydroxide is added, the mixture warmed to about 50°, and then drop by drop a solution of iodine in potassium iodide until a brown colour is produced. The solution is then carefully decolourised by addition of potassium hydroxide. On standing crystals of iodoform separate

For the estimation of alcohol the density of the chloroform forms an approximate guide provided the chloroform is otherwise pure, but for more exact determinations the method of Nicloux (Bull Soc chim [3] 35, 330, 1906) as modified by Béhal and François (J. Pharm. Chim. [6] 5, 417) is recommended The alcohol is removed from the chloroform by agitation with sulphuric acid, the latter is diluted and gently distilled The distillate is boiled with sulphuric acid and potassium dichromate solution containing 16·97 grams per litre is added until a green (not greenish yellow) tint is obtained. Each 2 c c. of solution equals 0·01 gram. of absolute alcohol. If the solution contains more than 2 p c of alcohol it must be diluted and the estimation repeated A similar modification has been suggested by Budde (*loc. cit.*). A. J. E.

1-CHLORO - 8 - NAPHTHOL - 3 : 6 - DISULPHONIC ACID
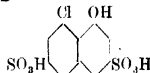
is prepared by dissolving 1-amino-8-naphthol-3 : 6-disulphonic acid in a cooled solution of sodium carbonate, carefully acidifying with hydrochloric acid and diazotising with the theoretical amount of sodium nitrite. The separated diazo-compound is warmed with hydrochloric acid and cuprous chloride, the copper removed by sulphuretted hydrogen, and the filtered solution saturated with common salt when the acid sodium salt of the chloro-acid is precipitated (Cassella & Co., D. R. P. 79055). The chloro-acid is also formed by treating 1 : 8-naphthylene-diamine-3 : 6-disulphonic acid with sodium nitrite in acid solution and acting on the azimino-compound with copper paste (Badische Anilin und Soda Fabrik, D. R. P. 147852).

CHLOROPHENINE ORANGE v. Azo-COLOURING MATTERS.

CHLOROPHENINE YELLOW v. PRIMULINE AND ITS DERIVATIVES.

CHLORORUBINE v. MADDER.

CHLOROXYLONINE $C_{22}H_{23}O_7N$, an alkaloid occurring in East Indian satinwood (*Chloroxylon Swietenia* (DC.)). It crystallises from alcohol in colourless prisms, m.p. 182°-183°, $[\alpha]_D^{18} - 9°$ 18', in chloroform, is soluble in excess of ammonia solution, and is neutral to litmus. The salts are crystalline and dissociate in water; aurichloride $B \cdot HCl \cdot AuCl_3$ groups of reddish-yellow needles, m.p. 70°. Chloroxylonine contains four ·OMe but no hydroxyl groups (Auld, Chem. Soc. Trans. 1909, 95, 964). It produces dermatitis when applied to the skin and is the cause of the dermatitis sometimes experienced by satinwood workers (Cash, Brit. Med. J. 1911, Oct. 7; and Bull. Imp. Inst. 1911, 9, 351).

CHLORPICRIN (*trichloronitromethane*) $CCl_3 \cdot NO_2$ is prepared by distilling nitro-compounds (in particular, picric acid) with bleaching-powder solutions (Stenhouse, Ann. 1848, 66, 241), by long heating of chloroform with fuming nitric acid (Mills, Ann. 1871, 160, 117), or by the action of chlorine on nitranilic acid (Levy, Jedlicka, Ann. 1888, 249, 86).

In Hofmann's method of preparation 45 parts of fresh bleaching powder are made into a paste with water and mixed with a saturated solution of 4·5 parts of picric acid in water at 30°. As soon as the very violent reaction is finished, the chloropicrin is distilled over (Ann. 1866, 139, 111).

Chlorpicrin is a mobile liquid which boils at 111·9°C. and possesses a specific gravity 1·69225 (0/4°) Thorpe. On heating it slightly decomposes into carbonyl chloride and nitrosyl chloride $(Cl_2 \cdot NO_2 \rightarrow COCl_2 + NOCl)$ (Gardner and Fox, Chem. Soc. Trans. 1919, 1188). On strong cooling it solidifies and then melts at −69·2°C. Its vapour acts as a strong irritant to the eyes and mucous membrane. For thermal expansion, *see* Thorpe, Chem. Soc. Trans. 1880, 37, 198. On reduction with iron and acetic acid it yields *methylamine*. A similar bromo-nitro-methane is known. It melts at 10°C., boils at 127° (118 mm.), and is converted by the action of potassium cyanide in cold alcoholic solution into the dipotassium salt of 1 1·2·2· tetranitroethane (Scholl, Ber. 1898, 31, 642; *ibid.* 1902, 35, 4292).

CHLORYL. Syn. for ethyl chloride used as an anæsthetic.

CHOCOLATE is a mixture of cacao paste with sugar and flavouring matter. The paste is prepared from fermented cacao beans (the unfermented kinds being unsuitable for chocolate making) in the manner described under COCOA. The sugar, which constitutes 50 p.c. or more of the mixture, consists usually of white crystals (although the lower-grade coloured sugars may be used for the cheaper chocolates), ground to the finest powder and completely dried before admixture with the cacao paste. The most common flavouring substance is vanilla, but other spices, as cardamoms, cinnamon, cloves, mace, and nutmeg, or the essential oils extracted from them, also artificial flavourings such as vanillin, are frequently employed. Peru balsam and gum benzoin are sometimes used for a similar purpose. The flavourings are introduced either in alcoholic solution or incorporated with sugar moistened with a little oil.

It is essential that during admixture the paste should be kept in a liquid condition, and to this end the mixing machines are heated to a temperature slightly above the melting-point of cacao butter, say from 35° to 40°, and the added sugar may be previously warmed with advantage to obviate a fall in temperature of the liquid cacao paste.

The various characters of French, Spanish, Swiss, and other chocolates depend upon the nature and proportions of the different ingredients used. A number of recipes for the preparation of some of the principal types of chocolate are given in Zipperer, 156.

In addition to sugar, various farinaceous substances are frequently employed in the cheaper forms of chocolate, as wheat and potato flour, rice, arrowroot and dextrin, and occasionally barley, oats, rye, and chestnut flour. In special cases where sugar is inadmissible, as in chocolate intended for use by diabetic subjects, the sugar is replaced by saccharin (*q.v.*). It is then usual, in order to give the necessary 'body' to the chocolate, to add some form of meal or flour (preferably leguminous); and pea, bean, or linseed meal are preferred for this purpose. *Nut chocolate* is made by adding nuts, either ground or whole, to the chocolate paste; and *milk chocolate* by incorporating with it 'milk powder,' *i.e.* milk deprived of its moisture and fat. The usual composition of milk chocolate, by the best makers, is approximately 10 p.c. cacao, 25 p.c. cacao butter, 40 p.c. sugar, and 25 p.c. dried milk. The above-mentioned forms of chocolate, after being ground into a more or less homogeneous mass, are placed in moulds to form bars, blocks, cakes, and numerous fancy shapes.

An immense variety of fancy preparations of chocolate consist, however, merely of a chocolate envelope containing other substances, as biscuits, creams, dried fruits, nuts, fruit jelly, liqueurs, &c., and in some cases, medicinal preparations, as chocolate-coated pills. The most important of these fancy preparations are the chocolate creams.

The so-called 'cream' is made either from powdered loaf sugar heated until it melts, or a mixture of this with glucose, with or without various colouring and flavouring materials. While in a liquid state, it is poured into moulds of the desired shape, made in starch flour on a table, which can be kept cool and which can be agitated by mechanical means. On cooling, the creams set into a stiff granular mass, when they are either dipped into a liquid chocolate paste, or the latter is poured over them by hand and spread uniformly by means of the rocking table. The process of covering, as well as most of the other processes in the manufacture of chocolate, are now generally effected by means of ingenious and complicated machinery.

An extra amount (about 15 p.c.) of cacao butter (or substitute) is added to the chocolate intended for covering purposes, to keep the latter in a sufficiently plastic condition during the process of cooling and to give smoothness to the finished article. The latter, whether in the form of plain chocolate or chocolate confections, should be quickly cooled, and attention to temperature is important throughout all the various operations.

The adulterants commonly used in chocolate are similar to those mentioned under COCOA.

the most important being the replacement of the cacao butter by other fats and oils (as coco-nut fat, illipé butter, &c.), the addition of various farinaceous substances, including dextrin, and the admixture of finely ground cocoa shells. (Zipperer. Die Shokoladen Fabrikationen ; Villiers et Collin, Traité des Substances Alimentaires.)

J. C.

CHOCOLATE FATS. Under this name, the writer comprises those vegetable fats which are used in the manufacture of chocolate as cacao butter substitutes. The natural chocolate fat is cacao butter, and best chocolates contain cacao butter only. 'Cheap' chocolates are made, to a larger or smaller extent, if not entirely, with substitutes At first, animal fats were used, but as they impart an unpleasant flavour ('animal flavour') to the chocolate, at present fats of vegetable origin only are employed, such as coco-nut stearine and palm-nut stearine. During recent years, attempts have been made to produce chocolate fats from Borneo tallow, dika fat, and similar vegetable fats.   J. L.

CHOLEIC ACID *v.* Cholic Acid.

CHOLESTEROL $C_{27}H_{46}O$. Discovered by Conradi in gall-stones in 1775. Occurs in all vertebrates and throughout the whole of the animal kingdom with the exception of certain groups of the invertebrata in which it is replaced by closely related substances (Dorée, Biochem J. 1909, 4, 72). It is found in bile, blood, the brain, and generally in all animal tissues, being closely associated with the lipins and fat present in the various organs Biliary calculi are composed almost entirely of cholesterol Its most abundant source is, however, wool grease

It may be obtained from animal tissues by the following method : the tissue is minced, dried in an oven at 100° and the dried material ground to a powder in a coffee mill and extracted in a Soxhlet apparatus with ether for 9 hours After distilling off the ether, the residue is saponified with alcoholic potash The alcohol is distilled off and the cholesterol separated from the soaps and glycerol by extraction with ether. The tendency of the ether and soap solutions to form emulsions makes the extraction difficult and various methods have been introduced to overcome this difficulty. Thus Ritter recommends that the soap residue be mixed with sodium chloride and water, evaporated to dryness and the resultant mass, after drying in an oven at 80°, extracted in a Soxhlet apparatus for 9 hours. Kossel and Obermüller (Zeit physiol. Chem. 1890, 14, 599) recommend saponification of the ethereal solution of fat with an alcoholic solution of sodium ethylate at ordinary temperature. After a short time a compact mass of soaps separates which is easily filterable, the cholesterol being present in the alcohol-ether filtrate. By this method wool grease, which is only saponified with difficulty, is completely decomposed in 24 hours at ordinary temperature. After filtering off the soap and washing the precipitate with ether, the filtrate is well washed with water, the ethereal solution dried with CaCl₂, and the ether distilled off, leaving a residue of cholesterol. It may also be separated from the fatty acids in wool grease by distillation with superheated steam or by direct heating (Mayer, Eng. Pat. 20639 ; J. Soc. Chem. Ind. 1894, 162).

Cholesterol crystallises from ether or chloroform in silky needles, m.p. 148·4 to 150·8 (corr.). From aqueous alcohol (90 p.c.) it crystallises in characteristic plates with one molecule of water of crystallisation. Insoluble in water, sparingly soluble in cold, easily in boiling alcohol (9 parts alcohol, sp gr. 0·87), and in chloroform, ether, carbon disulphide, less soluble in acetone, petroleum, benzene, and glacial acetic. Soluble in fats, fatty acids and in solutions of bile salts. Sp gr. 1·046 ; it is optically active ; in ether solution $(\alpha)_D = -31·12$; in $CHCl_3$ $(\alpha)_D = -36·61$. It sublimes unchanged at 200°, but is decomposed at higher temperatures, hydrogen being evolved at 300° to 320°. In a vacuum it can be distilled unchanged.

Constitution — Cholesterol is an unsaturated secondary alcohol, possessing a complicated terpene-like structure which has not yet been completely elucidated It has, however, been possible to establish in the molecule the presence of (1) a secondary alcohol group in a reduced ring ; (2) a terminal vinyl group: and (3) an isoamyl group On present knowledge is best represented by the formula
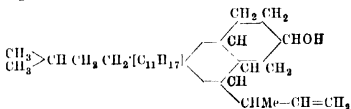
By applying various reagents under different conditions, a large number of oxidation products have been obtained (Mauthner and Suida, M. 24, 489 ; Windaus, 25 papers in Berichte, 1903 to 1917 ; Diels and Abderhalden, Ber. 1903, 3177 ; 1904, 3092 ; 1906, 885, 1371), the formula arrived at for cholesterol being based on these results. Oxidation of the secondary alcohol group gives the corresponding ketone, *cholestenone*, m.p. 78° ; the latter compound has also been obtained by direct oxidation of cholesterol with copper oxide at 300°, more conveniently by oxidising cholesteryl-di-bromide with chromic acid in acetic solution at 70°, and subsequently removing bromine by zinc and acetic acid (Windaus, Ber. 1906, 518). Cold chromic acid or potassium hypobromite solution oxidises the secondary alcohol to the ketone group and at the same time the vinyl group is oxidised and a new ring formed ; the diketone, *oxycholestenone* is the resulting product.

By the action of two hydrogen atoms to oxycholestenone, *cholestanedione*, m.p. 170°–171°, is produced. Fuming nitric acid reacts with cholesterol forming a nitro-compound which is reduced to *cholestanonol*, m.p. 140° (Windaus, Ber. 1903, 3752, 1917, 133), the latter being oxidised by chromic acid to cholestanedione. The relation of these substances to each other is shown by the following formulæ :

Cholesterol.   Cholestenone.

$\overset{|}{C}\diagdown$ CO	$\overset{|}{CH}\diagdown$ CO	$\diagdown$ CH $\diagdown$ CO
CO CH	CO CH$_2$	CHOH CH$_2$
Oxycholestenone	Cholestanedione.	Cholestanonol
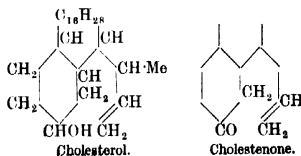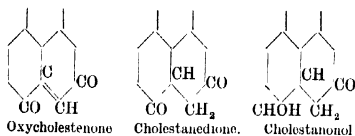
Further oxidation of these products has resulted in the isolation of a number of carboxylic acids, respectively mono, di, tri, and tetrabasic, some containing the same as, and some a smaller number of carbon atoms than cholesterol in their molecules.

The following compounds have been recognised among the products of the oxidation of cholesterol by nitric acid: dinitroisopropane and acetic, succinic, methylsuccinic and a-methylglutaric acids, acetone, hydroxyisobutyric acid, methylisohexyl ketone, and octane all of which substances may be regarded as derived from an isooctyl side chain in cholesterol On this assumption cholesterol may be represented by the formula

CHMe CH$_2$·CH$_2$

CH$_2$·CH CH CH CH$_2$ CHMe [CH$_2$]$_3$·CHMe$_2$

CH$_2$ CH —— CH CH CH$_2$

CH$_2$ CH(OH) CH CH·CH
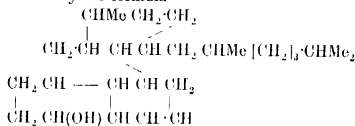
(Windaus, Zeitsch. physiol. Chem. 1918, 102, 160 ; Chem. Zents 1920, i, 82).

The action of ozone has been investigated by Dorée & Gardner, Molinari and by Harries. If the above constitution be accepted, only 4 atoms of oxygen should be taken up by the cholesterol molecule ; an ozonide containing 7 atoms of oxygen has, however, also been isolated. The balance of chemical evidence being against the presence of two double bonds in the molecule, Dorée and Gardner regard the addition of the three extra atoms of oxygen, which are only slowly taken up, as probably due to the opening of a bridged ring in the molecule.

From the first of the above formulae, only one dihydro derivative of cholesterol should be expected ; several have been described, none of which appears to be identical with coprosterin, the dihydro cholesterol occurring in the intestines. The β cholestanol, m.p. 142°, obtained by reducing cholesterol with platinum and hydrogen represents probably the true dihydro derivative (Willstatter & Mayer, Ber. 1908, 2199).

Cholesteryl Esters.—The cholesteryl esters of the lower fatty acids are prepared by heating cholesterol with the anhydrides of the acids, those of the higher fatty acids by boiling cholesterol with the acid and removing the water formed (Jaeger, Rec. trav. chim. 1907, 311). M.p. acetate, 114°, propionate, 98°. These substances on melting form anisotropic liquids, many of the esters having 3 stable liquid phases. The benzoate melts at 146° to a turbid liquid which examined with the polariscope shows definite crystal structure and at 178° passes to a clear liquid. The laurate is an instance of a compound which can be heated several degrees above its melting-point without melting.

Detection and Estimation.—The thin rhombic plates of cholesterol obtained from 90 p.c. alcohol are very characteristic. Under the

microscope they often show notched angles and exhibit a curious overlapping arrangement. A number of colour reactions have been described of which the following are the most useful : *Salkowski's test.* A small amount of cholesterol is dissolved in 2 c.c. chloroform and shaken with an equivalent amount of conc. H$_2$SO$_4$; the chloroform first becomes blood-red, then cherry-red, and finally purple, which lasts for several days ; poured into a basin, it becomes successively blue, green, and yellow owing to absorption of water. The H$_2$SO$_4$ layer is strongly fluorescent.

Burchardt-Liebermann Test.—Dissolve a little cholesterol in 2 c c. chloroform, add 20 drops of acetic anhydride and 1 drop conc. H$_2$SO$_4$: a violet-pink colour appears. This test is also given by resinic acids.

Estimation.—In animal tissues, the cholesterol may be estimated in the residue from the ether extract by converting to the acetate by boiling with acetic anhydride. The acetate is washed with water till free from acetic acid, and a weighed amount saponified with a known volume of alcoholic potash. The residual potash is titrated with standard acid and the amount of potash equivalent to the cholesterol thus determined. The iodine value will also give information. The most satisfactory method is that in which the cholesterol is precipitated and weighed as its insoluble compound with digitonin. Ransom, in 1901, found that the hæmolytic power of saponin is prevented by the addition of cholesterol. Windaus investigated the reaction (Ber. 1909, 238) and found that digitonin formed an insoluble compound with cholesterol in alcoholic solution. A 1 p.c. solution of digitonin in 96 p.c. alcohol is added to the ether-alcohol solution of fat, and after standing for some hours the precipitate is collected on a Gooch filter, washed with alcohol and ether, dried at 100°and weighed. The precipitate contains 25 p c. cholesterol. The filtrate is concentrated and after the addition of water extracted with ether ; the excess of digitonin remains in the weak alcoholic liquid, and the cholesteryl esters in the ethereal layer. The solvent is distilled off and the residue saponified with hot alcoholic potash. The cholesterol is then extracted with ether or petroleum and precipitated with digitonin as above described. In this way the free and combined cholesterol are separately estimated. Various modifications of this method have been introduced, thus Prescher recommends that after saponification, the soap should be decomposed with hydrochloric acid, CHCl$_3$ added, and the CHCl$_3$ solution of the fatty acids separated, filtered, and treated with the 1 p.c. digitonin solution at 50°, the liquid being stirred during the precipitation (Zeitsch. Nahr. Genussm. 1917, 481). In fats where adulteration with vegetable fats may have taken place, it is important to discriminate between phytosterol and cholesterol ; for this, the acetates or di-bromides must be prepared, and their melting-points examined. Marcusson and Schilling recommend the following method (Chem. Zeit. 1913, 1001), 50 grams fat are shaken for 15 minutes in a separating funnel with 20 c.c. 1 p.c. alcoholic solution of digitonin. The bottom layer of oil is run off ; the alcoholic upper layer containing the flocculent precipitate.

of digitonide is shaken with 50 to 100 c.c. ether. The ppt. is washed with ether, dried, powdered and again washed. It is then heated with 1·5 c.c. acetic anhydride in a test tube for half an hour. On cooling cholesterol and phytosterol acetates crystallise out. The acetates are re-crystallised and their m.ps. determined. Cholesteryl acetate melts at 114°, phytosterol acetate at 128°. They may also be separated by crystallising their di-bromides from ether and glacial acetic (Windaus, Chem Zeit. 1906, 1011). A mixture of 4 grams cholesterol and 4 grs. phytosterol was dissolved in 80 c.c ether and 80 c.c. 5 .p.c. bromine in glacial acetic solution added. After standing for 1 hour at 0°, the ppt. is washed with 40 c.c. glacial acetic acid, and with 40 c.c. 50 p.c. acetic acid, the washings being added to the filtrate, and a further ppt. added to the original ppt., which is then washed with water and dried. The ppt. contains the cholesterol bromide, the filtrate the phytosterol compound. The ppt. is heated with 100 c c. glacial acetic acid and 5 grs. zinc dust for 2 hours, the excess of zinc filtered off, and a large quantity of water added. A precipitate forms which is boiled for 2 hours with 100 c.c. alcoholic potash, and the cholesterol then precipitated by the cautious addition of water. The phytosterol is obtained by similarly treating the solution of the phytosterol bromide.

Cholesterol is found in commerce under the name of *lanolin* and is used mainly for medicinal purposes, and, owing to the ease with which it is absorbed by the skin, as a substitute for vaseline or lard in the composition of plasters, ointments and salves. It has also been employed in the manufacture of cosmetics and pomades, and for softening leather. Lanolin is obtained from wool oil, which contains about 70 p.c. of cholesterol and 30 p.c. fatty acids, by saponification by means of caustic soda, whereby an emulsion is obtained which on dilution with water gives so-called wool-milk. On treating in a centrifugal machine impure lanolin separates out as a cream and may be precipitated by lime. The purified product is afterwards kneaded with 30 p.c. of water, in which state it is found in commerce and forms the ' Hydrous Wool Fat ' of the ·B.P. Anhydrous lanolin absorbs about 100 p.c. of water, does not become rancid, and is antiseptic.

Isocholesterol is an alcohol isomeric with cholesterol which occurs only in woolgrease, m.p. 137–138°, $a_D = +60$. The mixture of cholesterol and isocholesterol is heated for 30 hours in a sealed tube with four times its weight of benzoic acid. The benzoates are insoluble in boiling rectified spirit and are separated by crystallising from ether. Cholesteryl benzoate crystallises in shining plates, its isomer as a light powder, m.p. 190°–191°. Isocholesterol may also be separated from cholesterol by means of oxalic acid ; cholesterol forms a crystalline compound with oxalic acid, and the isocholesterol can be estimated in the filtrate as benzoate (Madinaveitia & Gonzalea, Anal. Fis. Quim. 1916, 398). Isocholesterol gives no colour reaction with chloroform and sulphuric acid, but like cholesterol gives a pale yellow substance when heated with a drop of concentrated HNO_3 and a deep yellowish red colour on the addition of ammonia (Schiff's reaction).   I. S M.

CHOLESTROPHAN v. **PARABANIC ACID** .

CHOLIC ACID $C_{24}H_{40}O_5$. Occurs in bile, chiefly in combination with taurin and glycocoll as taurocholic and glycocholic acids. Free cholic acid, probably derived from these complex acids, occurs in small quantity in the intestinal contents, in the fæces and in the bile.

Preparation.—Cholic acid and the closely related isomeric choleic and desoxycholeic acids $(C_{24}H_{40}O_4)$ are prepared from bile after first treating it with alkali to decompose the compounds with glycocoll and taurin. Five kg. ox bile are boiled for 30 hours with 1 kg. 30 p.c. NaOH solution under a reflux condenser, 5 litres of water added and the mixture precipitated with hydrochloric acid at 50°. The precipitate is well rubbed up with water to remove hydrochloric acid and dried on a water-bath (Bondi and Muller, Zeitsch. physiol. Chem. 47, 501). The residue consists of a mixture of cholic acid with choleic and desoxycholeic acids, which may be separated in various ways, depending on (*a*) the sparing solubility of the barium salt of choleic acid, this being precipitated when barium chloride solution is added to a solution of the ammonium salts of the mixed acids · and (*b*) the relative insolubility of cholic acid in alcohol. Langheld (Ber. 1908, 378) recommends the following method : The crude dried acids are shaken with twice their weight of alcohol and the remaining cholic acid twice recrystallised from absolute alcohol. Excess of soda is added to the mother liquor, and the reaction mass warmed on the water-bath ; a nearly quantitative separation of sodium cholate takes place. This is filtered whilst hot, washed with boiling alcohol and recrystallised. The mother liquors are concentrated *in vacuó* and cooled : the sodium salts of the fatty acids present now separate The remaining acids are regenerated from the salts and esterified with 0·2 p.c. alcoholic HCl. The esters are boiled with much ligroin which dissolves 4 p.c. On saponifying the ligroin-insoluble esters with alcoholic potash, a further separation of cholic acid as sodium salt takes place. The residue is extracted with boiling benzene and ether, and then recrystallised from ethyl acetate. It consists of the two isomeric desoxycholeic acids the existence of which has been described by Mylius and by Vahlen. By fractionation from ethyl acetate these were obtained as substances melting respectively at 172° and 187°. The latter appears to be identical with the choleic acid obtained by Mylius (Ber. 1886, 369 and 2000 ; 1887, 683 and 1968).

Properties.—Cholic acid is a monobasic acid containing two primary and one secondary alcohol groups. It crystallises from aqueous ether or from dilute acetic acid with 1 molecule of water, from alcohol with one molecule of alcohol ; it loses both water and alcohol at 120°. It is soluble in acetone and acetic acid, almost insoluble in cold water, more soluble in hot (1 in 75). Its solubility in cold 70 p.c. alcohol is 1 in 20. Specific rotation : $a_D = 37·0$ (Vahlen, Zeitsch physiol. Chem. 21, 265). It behaves to bromine and potassium permanganate as a saturated substance, but forms an ozonide on treatment with ozone, suggesting the presence of an unsaturated cyclic substance (Langheld, Ber. 1908, 1023 ; von Furth and Ishihara,

Biochem. Zeitsch. 43, 323). A large number of oxidation products have been obtained (Pregl. Zeitsch. physiol. Chem. 1910, 167). On distilling under 12 mm. pressure, a heavy oil passes over at 200° to 300°, solidifying to the triply unsaturated cholatrionecarboxylic acid $C_{24}H_{34}O_2$, m.p. 163°. This acid gives the fluorescence with H_2SO_4 characteristic of cholic acid, but this property is lost on reducing it with hydrogen and palladium black (Wieland and Weil, Zeitsch. physiol. Chem. 80, 287).

Colour Reactions.—(1) Cholic acid dissolves in conc. H_2SO_4 with a reddish yellow colour showing a characteristic green fluorescence. (2) Pettenkofer's Test. An aqueous solution gives a red colour with a small amount of cane-sugar on addition of conc. H_2SO_4 or H_3PO_4. (3) Mylius' iodine reaction (Zeitsch physiol. Chem. 1887, 306). To 0 04 gr in 1 c.c. alcohol, add in the cold 2 c.c. N/10 iodine solution and slowly dilute with water, the mixture suddenly solidifies to a paste of crystals which appear intensely'blue by transmitted light. This test differentiates cholic from choleic and desoxycholeic acids.

Compounds with Glycocoll and Taurin.—Both cholic and choleic acids occur in combination with glycocoll and taurin forming the important bile-acids. In man the ratio glycocholate : taurocholate varies from 5 : 1 to 10 : 1. Taurin is present in the bile of most mammals, reptiles, birds and fishes. Glycocholate is absent in the bile of the polar bear, dog, goose, and in certain fishes. Cholic acid is formed in the liver and there combined with taurin and glycocoll It is probable that it is derived from the cholesterol of the red blood corpuscles.

The physical properties of these acids play an exceedingly important part in the digestive processes. They act as solvents for lipins and fat and so increase the velocity of resorption of the fatty acids in the intestine, and act as activators to certain enzymes.

Glycocholic Acid $C_{26}H_{43}O_6N$ occurs in quantity in bile, especially in that of herbivora. It is extracted from fresh bile by saturating with ether and decomposing with from 3 to 4 p.c. conc. HCl ; on standing a crystalline paste of glycocholic acid separates. The bile may also be dried on the water-bath and extracted with 90 p.c. alcohol After distilling off the alcohol the residue is taken up with water, neutralised with milk of lime and filtered. On acidifying with sulphuric acid the acid separates. It is easily soluble in acetone and acetic acid, soluble with difficulty in ether and insoluble in chloroform and benzene. According to Knoop, it crystallises with $1\frac{1}{2}$ mol. water of crystallisation and melts at 138°.

Taurocholic Acid $C_{26}H_{45}NSO_7$. This is the chief constituent of dog's bile. Alcohol is added to dog's bile and the filtered liquid concentrated to dryness on the water-bath. The residue is dissolved in alcohol, precipitated with ether and dissolved in water. Ferric chloride solution is added to the neutral solution until further addition produces no precipitate. After removing the iron, the filtrate is evaporated to dryness. The sodium salt is rubbed up with alcohol containing 2–3 p.c. hydrochloric acid ; after filtering off sodium chloride ether is gradually added until crystallisation sets in.

Properties.—Soluble in water, alcohol, ethyl acetate, insoluble in ether and chloroform. The crystals are obtained anhydrous on drying *in vacuô.* It melts with decomposition, the m.p. gradually changing from 100° to 180°. It precipitates protein from solution. I. S. M.

CHOLINE AND RELATED SUBSTANCES.

Choline, trimethyl β-hydroxyethyl-ammonium hydroxide, $CH_2(OH)\cdot CH_2\cdot N(CH_3)_3OH$, is formed by the hydrolysis of lecithin and hence probably occurs in all living cells ; its isolation from animal or vegetable tissues has been recorded very many times, but has no special significance, for even when not originally present in the free state, some is generally formed from phosphatides during the process of isolation. Kauffmann (Zeitsch. physiol. Chem. 1911, 74, 175) has shown, however, that if perfectly fresh ox brain is worked up rapidly, with precautions, hydrolysis may be avoided and then no choline is obtained. The best *natural source* is crude lecithin. Hard egg-yolk is extracted with ether and then with alcohol ; the extracts are mixed and evaporated and the residue is boiled for one hour with 50 parts of cold saturated baryta solution. After removal of the baryta and evaporation, the residue is extracted with absolute alcohol and to the solution alcoholic mercuric chloride or platinic chloride is added. (Compare D. R P. 193449 ; Moruzzi, Zeitsch. Physiol. Chem. 1908, 55, 352 ; MacLean, *ibid.* 55, 360.) The mercurichloride is decomposed by hydrogen sulphide, the platinichloride by the calculated quantity of potassium chloride ; in either case the choline chloride is extracted by absolute alcohol from the residue after evaporation. Most other natural sources yield very little choline (seeds and animal viscera something like 0·02 p c.). The isolation of choline (and betaine) from vegetable sources has been described by Schulze (Zeitsch. physiol. Chem. 1909, 60, 155). The aqueous plant extract is purified with lead acetate, and then, after removal of the lead acetate and evaporation, the residue is extracted with absolute alcohol. Choline and betaine are precipitated with alcoholic mercuric chloride. After reconversion into the chlorides and evaporation, cold absolute alcohol dissolves choline chloride, and leaves betaine chloride behind.

Choline is best prepared synthetically. Gaseous trimethylamine is made to act (*a*) on ethylene oxide (Wurtz, Compt. rend. 1867, 65, 1015 ; ' névrine '=choline) ; (*b*) on ethylene dibromide ; the resulting trimethylamino-bromethylium bromide is best converted into choline by heating with water (Krüger and Bergell, Ber. 1903, 36, 2901) ; (*c*) on ethylene chlorohydrin (Renshaw, J. Amer. Chem. Soc. 1910, 32, 128). Choline is also obtained (*d*) by methylating amino-ethyl alcohol (*see below* and Trier, Zeitsch. physiol. Chem. 1912, 80, 409). Of these methods (*c*) is the best ; rather more than one equivalent of trimethylamine gas is passed into ethylene chlorohydrin in a tube cooled to $-12°$ to $-20°$, which is subsequently heated to 80°-90°. The yield is almost quantitative.

The estimation of choline (and betaine) has been worked out by Staněk (Zeitsch. physiol. Chem. 1905, 46, 280 ; 1906, 47, 83 ; 48, 334), and depends on the precipitation in sodium bicarbonate solution of choline periodide, by

a concentrated solution of iodine in potassium iodide. The weak base betaine is similarly precipitated from the filtrate after acidification. Minute quantities of choline may be estimated physiologically after conversion into the acetyl derivative (*see below*; also Guggenheim and Löffler, Biochem. Zeitsch. 1916, 74, 208; Fuhner, *ibid.* 1916, 77, 408).

Qualitatively choline is recognised as the dichroitic crystalline periodide (Florence's test for semen; Bocarius, Zeitsch. physiol. Chem. 1901, 34, 339; Rosenheim, J Physiol 1905-6, 33, 220), and by conversion into other salts The *mercuri-chloride* $C_6H_{14}ONCl,6HgCl_2,H_2O$, crossed hexagonal prisms, m.p. 249°-251° dissolves in about 50 parts of water at room temperature, but in alcoholic solution the limit of precipitation is given as 1·2,000,000. The *platinichloride* $(C_6H_{14}ON)_2PtCl_6$ dissolves in 5·82 parts of water at 21° and is dimorphous, the conversion of the regular isotropic form into the anisotropic monoclinic one is the surest means of detecting choline without analysis (Kauffmann and Vorlander, Ber. 1910, 43, 2735). The *aurichloride* dissolves in 75 parts of water at 21° and in hot alcohol. Neither this nor the platinichloride has a characteristic melting-point. The free base is a syrup, many of the salts are deliquescent (for details *see* Gulewitsch, Zeitsch. physiol. Chem. 1898, 24, 513). For soluble non-deliquescent salts, *see* Ger. Pats Nos. 290523 and 290740 (Chem. Soc. Abstr. 1916, i. 468 and 548) The physiological action of choline is in general antagonistic to that of atropine, and not very intense; intravenous injection lowers the blood pressure (*e g.* Mendel, Underhill and Renshaw, J. Pharm. exp Therap 1912, 3, 649). Esterification of the alcoholic hydroxyl enormously increases the activity. *Acetylcholine* is 100,000 times as depressant as choline (Hunt and Taveau, U S. Hyg. Lab. Bull No. 73, and physiological estimation above). Acetylcholine occurs in ergot (*q.v.*), but is very readily hydrolysed and is absent from most extracts. The *nitrous acid ester*, long regarded as 'synthetic,' or pseudo-muscarine, is formed by the action of concentrated nitric acid on choline. The demonstration by Ewins (Biochem J 1914, 8, 209) that the reaction product is not an aldehyde, as was commonly supposed, explains the differences in physiological action between it and muscarine from *Amanita muscaria*, the Fly Agaric. This natural product requires further investigation, for it is apparently not identical with botaine aldehyde as was supposed by its discoverers. The alkaloid *sinapin* in black mustard seeds is the choline ester of sinapic acid Many other choline esters and related derivatives have been prepared by Hunt and Taveau (*l.c.*), Menge (J. Biol Chem. 1911, 10, 399, and U.S. Hyg. Lab. Bull. No. 96), Ewins (Biochem. J. 1914, 8, 366), and by Fourneau and Page (Bull. Soc. chim. 1914 [iv.] 15, 544). The latter, in connection with the physiological action of snake venom, found that *palmityl* and *stearyl choline* are strongly hæmolytic.

Other bases related to choline are *neurine* or *vinyltrimethyl ammonium hydroxide*

$$CH_2:CH\cdot N(CH_3)_3OH$$
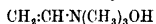
formed from choline by putrefaction and with a similar physiological action but 10-

20 times as toxic. *Amino ethylalcohol* or *hydroxy ethylamine* ('*colamine*') $CH_2OH\cdot CH_2NH_2$ was obtained by Thudichum in 1884 by the hydrolysis of the brain phosphatide kephalin, in which it entirely replaces choline. It has been more recently recognised in other phosphatides, Trier (Zeitsch. physiol. Chem. 1913, 86, 1, 141, 153, 407). For a full account of choline and allied substances, *see* Barger, The Simpler Natural Bases, Longmans, 1914 G. B.

CHOLINE ESTERS *v.* MUSCARINE and ERGOT.

CHONDRIN. A substance allied to and much resembling gelatin Obtained by boiling cartilage with water. When dried it is a hard, horny substance which softens to a jelly in cold water, and is entirely dissolved by boiling water. It is precipitated from its aqueous solution by nearly all acids, in excess of certain of which it redissolves; and by alum, lead acetate, copper and iron sulphates, and mercuric and mercurous nitrates. These reactions are said to distinguish it from gelatin.

By Morochowitz, chondrin is regarded as a mixture of gelatin, mucin, and salts (*v.* GLUE).

CHROMATOMETERS *v* COLORIMETERS.

CHROMAZONE BLUE,-RED *v.* AZO- COLOURING MATTERS

CHROME BLACKS, -DEEP BLACK, -BROWNS, -FAST BLACK, -FAST CYANINE, -FAST YELLOWS, -YELLOW, -ORANGE, -PATENT GREEN, *v* AZO- COLOURING MATTERS

CHROME VIOLET. Syn. *Mauveine, Perkin's violet* (*v.* AZINES AND COLOURING MATTERS). The term is also applied to the sodium or ammonium salt of aurintricarboxylic acid (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

CHROMITE or **Chrome-iron-ore.** A member of the spinel group of minerals, consisting essentially of ferrous oxide and chromic oxide $FeO\cdot Cr_2O_3$, or $FeCr_2O_4$, analogous to the aluminates. The ferrous oxide is, however, often partly replaced by magnesia, and the chromic oxide by alumina, so that there is a passage to chrome-spinel or picotite; on the other hand, with a replacement of chromic oxide by ferric oxide, there may be a transition to magnetite (Fe_2O_4 or $FeFe_2O_4$). All these minerals are cubic in crystallisation and belong to the same isomorphous group—the spinel group. The actual amount of chromic oxide varies considerably, as shown by the following analyses; the ordinary ore, as mined, contains on an average 45 p.c. Cr_2O_3:—

	Cr_2O_3	Al_2O_3	Fe_2O_3	FeO	MgO
I.	67·9	—	—	32·1	—
II.	44·15	22 41	5·78	11·76	15·67
III.	59·20	7·15	n.d.	25·02	4·42
IV.	41·23	24·58	2·28	16·99	14·77
V.	56 54	12·13	—	18·01	14·08

I. Calculated for $FeCr_2O_4$.
II. Franklin, Macon co., North Carolina.
III. Price's Creek, Yancey co , North Carolina (J. H. Pratt, Amer. J. Sci. 1899, vii. 281. Also SiO_2 2 80, MnO 0 69.
IV. Tampadel, Lower Silesia (H. Traube, Zeits. Deutsch Geol. Ges. 1894, xlvi, 50).
V. Dun Mountain, New Zealand.
(For analyses of chromite isolated from meteorites, *see* W. Tassin, Proc. U.S. Nat. Museum, 1908, xxxiv. 685.)

In general appearance, chrome-iron-ore is very like magnetite, but it is readily distinguished from this by the dark-brown colour of its streak

or powder, and by the fact that it is only slightly, if at all, magnetic. Sp.gr. about 4·5. Crystals are of rare occurrence, the mineral being usually found as grains disseminated in basic rocks of igneous origin, especially those rich in olivine (viz. the peridotites). Sometimes these grains are segregated into nodular masses of considerable size and with a granular to compact texture. Rocks of this kind, when subjected to weathering processes, become hydrated and altered into serpentine, and for this reason most of the workable deposits of chrome-iron-ore are in serpentine rocks. With the denudation and breaking down of these rocks, the heavy grains of the chemically resisting chromite collect in the beds of streams and rivers, and some of the deposits worked in the Ural Mountains are of this nature

Chromite is the only commercial source of chromium and its compounds. It is used for the preparation of the oxides and chromates employed as pigments, and in dyeing, calicoprinting and tanning; in the manufacture of chrome-steel and ferrochrome, and for chrome-bricks and furnace linings. It is mined in European and Asiatic Turkey, Greece, the Ural Mountains, New Caledonia, India, Baluchistan, Rhodesia, Quebec, California and Oregon; and formerly, to a considerable extent, at Bare Hills, near Baltimore in Maryland, and in Lancaster co. in Pennsylvania. Quarries were, at one time, worked on Unst, one of the Shetland Isles (Special Reports on the Mineral Resources of Great Britain, vol v Mem Geol Survey, 1916).

On the Californian deposits, *see* J S Diller, Mineral Resources of the United States, U S. Geol. Survey, for 1915, 1916 ; those of Canada, *see* F. Cirkel, Dept. of Mines, Canada, No 29, 1909 ; and those of Rhodesia, A E. V. Zealley, Trans. Geol. Soc. S. Africa, 1914, xvii. 60.

L. J. S.

CHROMIUM. (Fr. *Chrome*; Ger. *Chrom*) Symbol Cr. At wt 52 0. Chromium occurs principally as chrome-iron-ore, or *chromite* (*q.v.*). Found largely in Rhodesia, New Caledonia, Russia, Greece, Asiatic Turkey, and India. Chromite deposits are also worked to a small extent in Bosnia-Herzegovina, Japan, California, Oregon, Transvaal, and Newfoundland. The principal producers in 1913 were New Caledonia 62,000 tons, Rhodesia 63,000 tons, Russia 21,000 ; these countries furnishing about 90 p.c. of the world's total. As sesquioxide Cr_2O_3, it is found in small quantities in *chrome ochre*, generally mixed with clay and associated with chromite, in France and Siberia. As lead chromate it occurs in *crocoisite* and *melanchroite* $PbCrO_4$, and as a basic lead chromate in the rare mineral *phœnicite* $3PbO·2CrO_3$. It is usually present in the form of *chromite* in meteorites, but rarely to the extent of more than 1 p.c. The greenish colour of the emerald, verd-antique marble, serpentine, sapphire, and many other minerals, is due to the presence of chromium sesquioxide.

Preparation.—Metallic chromium may be prepared by several methods. Deville produced it in combination with a small quantity of carbon, in ingots weighing as much as 100 grams, by the ignition of a mixture of chromium sesquioxide and sugar in a lime crucible, at the highest temperature of a blast furnace.

Wöhler (Annalen, 111, 230) prepared chromium by fusing a mixture of the violet chromium sesquichloride with twice its weight of zinc under a layer of equal parts of potassium and sodium chlorides. The mixture of zinc and chromium so produced was treated with dilute nitric acid to remove the zinc, and the chromium remained as a light-greenish powder consisting of minute octahedra belonging to the quadratic system (Bolley), of sp gr. 6·81 according to Wöhler, 7·3 according to Bunsen.

Chromium may be prepared by the electrolysis of its salts, but the purity and condition of the deposit vary greatly with current strength and solution concentration. A bright deposit, capable of receiving a polish, can be obtained by the use of a hot 25 p c. acid solution of chromic chloride, with a current density of about 40-50 amperes per square foot. As, in the case of nickel, the deposits have a strong tendency to peel (Cowper Coles, Chem. News, 81, 16).

It is most easily obtained in small quantities by heating equivalent parts of chromic oxide (or mixture of the oxide and anhydride) with aluminium powder. When started, the heat of the reaction causes it to continue and a fused mass of chromium of a high degree of purity is obtained (Goldschmidt, Annalen, 301, 19).

In large quantities it is best prepared by heating the oxide with carbon in the electric furnace. The crude metal thus obtained always contains *carbides*, of which three definite compounds appear to exist: Cr_3C_2, Cr_4C, and Cr_5C_2. It may be refined by further heating in the electric furnace on a bed of lime mixed with chromic oxide. The refined metal crystallises in cubes or octahedra and still contains about 1·5 p.c. carbon. By further refining, however, with a double oxide of chromium and calcium, the pure metal is obtained (Moissan, The Electric Furnace)

Pure chromium is a steel-grey metal, slightly harder than glass ; the carbides, however, are harder than quartz, so that a metal with between 1 5 and 3 p.c. carbon can only be cut and polished by diamond dust. Its density is 6·92, and it oxidises superficially in moist air ; the melting-point is probably above 2000° (1510°, Johnston, J. Ind. Eng Chem. 1917, 9, 873). The pure finely divided metal burns rapidly when heated in the blowpipe flame, and a pyrophoric powder may be prepared by distillation of chromium amalgam *in vacuö* (*v. infra*). It also unites with nitrogen when heated in nitrogen or ammonia, forming a very stable *nitride*. Crude chromium does not burn until heated to above 2000°. It combines with sulphur vapour at 700°, and when heated to redness in hydrogen chloride, forms *chromous chloride.* Electrolytic chromium occludes 250 times its volume of hydrogen. Aqueous hydrochloric acid acts slowly on the metal, but the action is accelerated if the chromium is made the anode in electrolytic hydrochloric acid. Heating with sulphuric acid causes evolution of sulphur dioxide ; concentrated nitric acid and *aqua regia* have no action. As in the case of iron, *active* and *passive* varieties of chromium exist ; in general, the metal is rendered passive by oxidising solutions, whilst

hydrogen ions make it active. In the electro-motive series, the active chromium immediately follows zinc, the inactive metal is near platinum. The cause of the passive state is usually ascribed to the existence of a superficial film of oxide, but this view has been disputed.

Chromium carbide boils at 2270° C., and the vapour consists entirely of chromium. Between 2050° and 2250° the fused mass remains constant in composition and corresponds with Cr_3C_2. Below 2050° down to 1875° graphite and the carbide Cr_3C_2 exist side by side as solid phases. Cr_5C_2 is also shown to exist (Zeitsch. Elec. Chem. 18, 24. 157).

Alloys. Various alloys of chromium have been prepared, chiefly by means of the electric furnace, by the 'thermit' method, or by the mixture of the molten metals.

Molten *zinc* dissolves but little chromium, a hard and brittle alloy has been obtained in the form of hexagonal lamellæ. *Aluminium* and chromium mixtures, containing between 5 and 55 p.c. chromium, separate into two liquid layers, and probably contain a compound, Cr_3Al. The alloys with a low percentage of chromium are brittle, one containing 13 p c. chromium can be powdered in a mortar.

Alloys with *antimony* are brittle, and com-pounds represented by SbCr and Sb_2Cr are known. Chromium alloys with *copper* with difficulty, but an alloy can be obtained by stirring in copper oxide into a molten alloy of aluminium and chromium (Moissan). The liquid metals are miscible only to a small extent.

Cobalt and chromium are miscible in all pro-portions, both in the liquid and the solid states, and yield a mixture of minimum melting-point 1320° with 47 p.c Cr. Homogeneous alloys, containing above 30 p.c. Cr, when cooled, separate into two sets of crystals, distinguishable by electrolytic etching.

Nickel chromium alloys with less than 90 p.c. nickel are non-magnetic.

Silver and chromium, although partially miscible in the liquid state, form no solid solu-tion. Molten *cadmium* does not dissolve any chromium. Molten mixtures of *lead* and chromium, containing more than 27 p.c. lead, separate into this mixture and pure lead.

Chromium also forms *silicides* and *borides* in the electric furnace ; of the former, compounds represented by $SiCr_3$, $SiCr_2$, Si_2Cr_3, and Si_3Cr, have been described. They are very hard—$SiCr_2$ is harder than corundum—and are not attacked by ordinary acids, though attacked readily by hydrofluoric acid and by *aqua regia*. The *borides* Cr_3B_2 and CrB are metallic looking crystalline solids, not attacked even by a mixture of *aqua regia* and hydrofluoric acid. The com-pound CrB is stated to be weakly magnetic. The *phosphide* CrP, obtained from the metal and copper phosphide, forms dull-grey crystals, sp.gr. 5·71, which burn in oxygen, forming chromium phosphate, but are unattacked by all acids except a mixture of hydrofluoric acid and *aqua regia*.

By electrolysis of a strongly acid solution of chromic chloride, using a platinum anode and a mercury cathode, an amalgam Hg_2Cr is obtained, soft and brilliant, and altering but slightly in air. By pressure, a harder amalgam

HgCr is obtained, which alters in air more rapidly. By distillation *in vacuó*, both lose mercury and yield pyrophoric chromium (*v. supra*). An amalgam may also be obtained by the action of sodium amalgam on a chro-mium salt.

With *iron* the alloys of chromium are of great interest. The presence of chromium in iron or steel produces a much finer texture, greater hardness, tenacity, and elasticity, and greater smoothness of fracture. Chromium can-not be used to replace carbon in steel, as has been asserted (Boussingault).

When crystalline, the tendency of these alloys is to produce needles instead of plates, as in the case of manganese. Chromium lowers the Ar_1 point eventually causing its disappear-ance, whilst it raises the Ar_2 point of the steel, the proportion of chromium required being less the higher the carbon, *e.g.* with 0·2 p.c. carbon 5 p c. chromium is required. Hence chromium steels are self-hardening (*i.e.* air-hardening). Steels containing 15 p.c. chromium have been used for tools and have to be cast to shape. With 0·5 p c. chromium and 0·5 p.c. carbon the steel is used for well bits and jars and has no equal in the hardened state. With 1 p.c. chromium and high carbon the steel is used in bearing balls, cones, roller bearings and crushing machinery. These low chromium steels when well annealed can be machined Its principal use is in conjunction with other alloy steels, especially nickel steels, to which it imparts greater toughness and hardness. As such it is used extensively in automobile parts, and when used in armour plates they are case-hardened and quenched Chrome steel is also used in the manufacture of special kinds of files. The alloy is usually prepared of the requisite composition by the addition of a definite amount of 'ferrochrome,' containing from 40 to 85 p.c. chromium to the molten steel. Ferrochrome was formerly prepared from rich chrome-iron ores in blast furnaces by the use of coke and hot high-pressure blast, or in crucibles. In 1890 the manufacture was commenced in the electric furnace and has gradually superseded the other methods. In the reduction of chromium from chromite to form ferrochrome, the iron being reduced, reduction of chromic oxide begins about 1185° C. Thirty parts of pure carbon are theo-retically necessary for every 100 parts of iron and chromium reduced. On the basis of the double carbide Fe_3C,Cr_3C_2 being formed in reduction of the chromite the following reaction occurs :

$$9FeO,9Cr_2O_3 + 60C$$
$$= [2(Fe_3C,3Cr_3C_2) + 3Fe] + 36CO$$
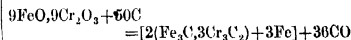
The ferrochrome resulting would contain theoretically 10·4 p.c. carbon, 31·4 p.c. iron, and 58·2 p.c. chromium. The ore has to be finely ground and is then mixed with anthracite coal in the proportion of 37 parts of carbon to 100 parts of ore which forms the above alloy and charged into the furnace. The power consumption in a 750 kilowatt furnace of the Alby carbide type at Kapperaen, Norway, was 3·0 kw. hours per pound, or 0·68 kw. year per short ton for 5 p.c. carbon and 65 p.c. chromium ferrochrome. The percentage of carbon in the ferrochrome cannot be kept low by regulating the coal

charged into the furnace, but decarburisation can be effected with an oxide slag of iron or chromium after tapping the slag from the first reduction. (Amer. Electrochem. Soc. 1913, 176.)

The addition of chromium decreases the magnetic properties, but all alloys, to 80 p.c. chromium, are magnetic. The magnetic property of chromium is not increased by cooling in solid hydrogen (Compt. rend. 150, 687). A *carbide* of *chromium* and *tungsten* of great hardness and of sp.gr. 8·41, has been produced in the electric furnace, and to it the special properties of *chrome tungsten steels* are probably due. These latter (as well as *chrome molybdenum steels*), containing up to 3 p.c. chromium and 16 p.c. tungsten, are used for the manufacture of machine tools. Cobalt is frequently added to both classes of tool steel.

Detection of Chromium. When heated strongly, all compounds of chromium impart a green colour to a borax bead in both the reducing and oxidising flames. On ignition with potassium nitrate, all chromium compounds produce a yellow colour, due to the presence of potassium chromate. If this is dissolved in water, the addition of a solution of lead acetate produces a precipitate of chrome yellow. A similar oxidation occurs when chromium compounds are fused with sodium peroxide, or when solutions of chromium salts are boiled with sodium peroxide. A delicate test for a soluble chromate is to add excess of hydrogen peroxide to a little of the solution in a test tube and shake up with a few c.c. of ether; a blue colouration indicates chromium. (*See* under Perchromic acid.)

Solutions of chromic salts or salts of sesquioxide of chromium have an acid reaction. With caustic alkalis they produce a green precipitate of hydrated oxide partially soluble in excess of the reagent, but reprecipitated on boiling the solution. With carbonates, a green precipitate is produced, likewise soluble in excess.

Chromates (in which the chromium exists as an acid) are usually strongly coloured. Soluble chromates are reduced, when warmed with sulphuric acid and a reducing agent such as alcohol, with the production of a green colour. The chromium is then present as a base, and may be precipitated, as already mentioned. When heated with hydrochloric acid, they are partially reduced, with evolution of chlorine and formation of chromium chloride and chloride of the metal present as chromate, together with the formation of *chromyl chloride* CrO_2Cl_2.

Solutions of chromates containing no free acid except acetic acid give a yellow precipitate with a salt of lead, a red precipitate with silver nitrate, and a yellow precipitate with a salt of barium.

Estimation.—When present as a base, chromium is usually estimated as sesquioxide Cr_2O_3. For this purpose, the solution is heated nearly to boiling, ammonia solution added in slight excess, and the temperature maintained until the liquid is perfectly colourless, indicating that the hydroxide, which is slightly soluble in excess of ammonia, is completely precipitated. The precipitate is well washed by decantation and transferred to a filter, washed thoroughly with hot water, dried, and ignited. The oxide produced

contains 68·63 p.c. of chromium. The precipitation is not complete in presence of organic matter, and when a glass vessel is used, the precipitate always contains a small percentage of silica. Chromium, when present as a chromate, cannot be estimated directly by that method. It requires to be first reduced to a base. For this purpose, hydrochloric acid and a small quantity of alcohol are added, and the solution heated until the odour of alcohol is dispelled. The chromium may then be precipitated as above. For the direct estimation of chromium in chromates, the precipitation with lead acetate is most satisfactory. The solution is mixed with sodium acetate and acidified strongly with acetic acid. A solution of normal lead acetate is then added, and the precipitate of $PbCrO_4$ is collected on a weighed filter, washed, dried at 100°, and weighed. It contains 16·19 p.c. of chromium, or 31·06 p.c. of chromic anhydride CrO_3. Or the precipitate may be dissolved in well-cooled dilute hydrochloric acid (1 of HCl to $3H_2O$) potassium iodide added and the liberated iodine titrated with N/10 sodium thiosulphate. The following scheme may be adopted for the estimation of chromium in chrome iron ore : A few grams of the carefully sampled mineral are ground in an agate mortar and passed through a fine muslin sieve. The dust so produced is further ground in small portions until all grittiness, on passing a little between the fingers, has disappeared and the ore cakes as an impalpable powder round the pestle. About 0·5 gram of the powder is weighed into a platinum crucible of about 50 c.c. capacity, covered with twelve times its weight of recently fused hydrogen potassium sulphate (potassium bisulphate), and gently heated to just fuse the sulphate. After keeping at this temperature for 15 or 20 minutes, the heat is gradually increased until the crucible bottom becomes red hot. The fused mass should not be allowed to rise above half-way up the crucible. The mixture soon fuses quietly, and evolves dense fumes of sulphuric acid ; the heat is gradually increased to bright redness. In about half an hour, 6 parts of powdered anhydrous sodium carbonate are added and the mixture again fused for an hour at a red heat, 6 parts of nitre being added in small portions. The temperature is then raised to a full red heat for about 20 minutes ; the crucible cooled and transferred to a porcelain basin where the mass is boiled out with water. The solution is filtered, and the residue washed with hot water until the filtrate comes through colourless. The filter and its contents are dried, the precipitate detached and placed with that still remaining in the basin, the filter paper burned, and the ash also added. To ascertain if the fusion has been satisfactory, this residue is digested with moderately strong hydrochloric acid, when the whole should dissolve. Any insoluble black residue indicates either imperfect grinding or insufficient fusion. It must be collected on a filter, dried, and the whole ignited in a crucible and treated with potassium bisulphate, &c., as in the first instance. The aqueous extract, after fusion, is mixed with the main solution. To the liquid, a few grams of ammonium nitrate are added, and the whole evaporated to dryness, taken up with water, and filtered from the alumina, silica, &c., into a porcelain basin. An excess of sulphurous acid solution is then

added, and the solution heated until that gas is nearly expelled. The chromate, having thus become reduced to chromium sulphate, a slight excess of ammonia is added, and the solution boiled until colourless. The precipitated chromium hydroxide is washed by decantation with hot water, transferred to the filter, and washed with hot water six times. The use of the suction pump is of great assistance in this operation. The precipitate and filter are then dried, transferred to a weighed platinum crucible, and heated gently until the paper is charred The crucible lid is then placed at the edge of the crucible so that the flame may reverberate into the crucible, and the whole ignited strongly for 10 or 15 minutes. The weighed precipitate should show no yellowish colour on treatment with a few drops of water; if such a colour is produced it indicates imperfect washing of the precipitate from alkali salts. The oxide contains 68·63 p.c. of chromium.

The oxidation may also be effected by means of sodium peroxide, and the chromate produced, instead of being reduced to chromic oxide, may be estimated as chromic acid volumetrically. For this, various methods are available, e.g : (1) boiling with standard arsenious oxide and estimating the excess by standard iodine; (2) adding potassium iodide and titrating iodine liberated by standard thiosulphate; (3) adding standard ferrous ammonium sulphate solution and titrating excess with standard potassium dichromate.

A speedy and accurate method for the estimation of chromium in ferrochrome or chromite, is the following: 1 part of the ore is finely powdered, as described above, and fused with a mixture of 5 parts of sodium peroxide and 8 parts of caustic soda in a silver crucible. The aqueous extract is filtered and again similarly treated; three or four such fusions are necessary to dissolve all the ore, when the only residue is a little silver extracted from the crucible. The filtrate is acidified with sulphuric acid, boiled for 40 minutes and diluted to a known volume An aliquot part is then titrated with potassium iodide and standard sodium thiosulphate.

Chromates may also be readily estimated in acid solution by hydrazine sulphate, whereby nitrogen is liberated, 100 c.c. of nitrogen at N.T.P. being equivalent to 0·59576 gram Cr.

COMPOUNDS OF CHROMIUM.

Chromium forms a number of oxides; of these, chromous oxide CrO, and chromium sesquioxide Cr₂O₃, are definite basic oxides, yielding with acids salts in which chromium is present as a divalent or trivalent cation, forming the chromous and the chromic salts. Chromic oxide can also combine with bases to form salts, the chromites, of the type MCrO₂, in which the chromium is present in the monovalent anion CrO′₂. Chromic anhydride CrO₃ is an acid anhydride forming, with bases, salts of the type M₂CrO₄, the chromates, or M₂Cr₂O₇, the dichromates, in which the chromium exists as the divalent anion CrO″₄ or Cr₂O″₇. Other oxides have been prepared and are usually regarded as compounds of the basic and acid oxides, e.g. Cr₂O₃·CrO₃=chromic chromate. The chromous salts are of no industrial importance at present.

The salts of chromium are coloured shades of

violet or green; all solutions of violet chromium salts show similar absorption towards light; spectrum due therefore to the chromium ion. In solutions of green complex salts the absorption band and limit of complete absorption are both shifted towards the red end of the spectrum.

Chromous oxide, CrO, is most conveniently prepared by the action of dilute nitric acid on chromium amalgam which dissolves the mercury leaving chromous oxide as a black powder.

Chromous salts. Traube & Goodson (Ber. 1916, 1679) have prepared chromous salts by the electrolytic reduction of the corresponding chromic salts as a cathode of pure lead. The most favourable conditions for the reduction of violet chromic salts are in moderately acid concentrated solutions with a current density of 2 5 amps. per square decimetre. The more common green salts can be used in more concentrated solutions, but require a greater density of current.

Chromous salts are gradually oxidised in acid solution with the liberation of hydrogen, thus 2CrO | H₂O=Cr₂O₃+H₂. They are on this account able to reduce compounds with double or triple linkings in the presence of water. Acetylene is thus reduced to ethylene, but not to ethane. Nitrous oxide in the presence of alkali hydroxide is reduced to nitrogen. Nitric acid and hydroxylamine are reduced quantitatively to ammonia (Ber. 1916, 1692). Chromous salts from stable double compounds with hydrazine salts and may be precipitated from chromous acetate dissolved in air free water, covered with petroleum ether. Chromous di-hydrazine chloride CrCl₂2N₂H₄ is a blue-coloured powder sparingly soluble in water.

Chromic oxide, *Chromium sesquioxide* Cr₂O₃. This compound is produced by the oxidation of metallic chromium and by ignition of chromic hydroxide, chromic anhydride, and certain chromates.

Wöhler prepared this oxide in fine, small rhombohedral crystals by passing the vapour of chromyl dichloride through a tube heated to redness. The crystals are isomorphous with corundum and of equal hardness; their sp.gr. is 5·21. Crystalline chromic oxide is also obtained when a mixture of potassium dichromate and sodium chloride is heated to redness (Ditte, Compt. rend. 134, 336). The finest coloured amorphous chromium oxide is produced by heating mercurous chromate Hg₂CrO₄ in a covered crucible; mercury and oxygen escape, and the oxide remains as a green powder. For the preparation of this substance on the large scale, a great number of methods are recommended.

Boil a solution of potassium dichromate with half its weight of flowers of sulphur so long as the green hydroxide is precipitated. The addition of a little potash solution, by forming potassium sulphide, accelerates the decomposition. The precipitate is filtered from the solution containing potassium sulphate, and washed. The sulphur retained in the precipitate may be removed by heating. Instead of performing the reaction in the wet way, the mixture may be ignited in a crucible, and the resultant mass digested with water (Lassaigne, Ann. Chim. Phys. [3] 14, 299). Wöhler (Pogg. Ann. 10, 46) heats a mixture of potassium

dichromate with its own weight of ammonium chloride and a small quantity of sodium carbonate, and purifies the residue by washing.

According to Barian (Rev. Scient. 20, 425), a very pure colour, suitable for colouring fine porcelain, is produced by igniting in a crucible a mixture of 4 parts of potassium chromate and 1 part of starch. The mass is washed free from potassium carbonate and re-ignited.

Chromic sesquioxide is a green pigment of great permanence. It is not acted upon by chlorine or sulphur gases or by an intense heat. It melts at 1990°, and crystallises on cooling.

Chromium hydroxide $Cr_4(OH)_5O_3,10H_2O$ or $Cr_4(OH)_{10}O, 9H_2O$ (Jovitschitsch. Heid. Chim. Acta, 1920, 3, 46) absorbs carbon dioxide from the atmosphere until saturation limit is reached. The compound appears to be $CO_3[Cr(OH)_5)_2,8H_2O$ or $\begin{matrix} Cr_2(OH)_5 \cdot O \\ Cr_2(OH)_5 \cdot O \end{matrix} CO,9H_2O$ (Jovitschitsch) It can be dried at 100° without losing CO_2, which is, however, liberated by acids. (Compt. rend. 158, 782.)

Hydrogen and carbon monoxide are without action, but it is reduced to the metallic state on heating with carbon at a temperature of 1185° or higher.

This oxide is largely used under the names *chrome green* (mixtures of *chrome yellow* and Prussian blue are also frequently called *chrome greens* and must not be confounded with the true chrome green), and *ultramarine green* for imparting a green colour to glass, porcelain, &c. It is used for producing the chrome red glaze in ceramic ware, as a pigment, in oil and water colours and in printing, and as a mordant in calico-printing and dyeing. Certain hydrated oxides are also used under various names ; their colours are, generally speaking, brighter than that of the anhydrous oxide, but they usually contain small quantities of other substances besides the oxide and water.

Guignet's Green ; *Pennetier's Green* ; *Emerald Green* ; *Veridian* $Cr_4O_3(OH)_6$. This pigment appears to be identical with that formerly manufactured in secret by Pennetier. According to Guignet's method, 3 parts of boric acid and 1 part of potassium dichromate are heated to dull redness in a reverberatory furnace. The mass swells up, evolves oxygen, and becomes of a fine green colour ; it contains the borates of potassium and chromium, or a double borate of those two metals. It is boiled with water, whereby the borate of chromium is decomposed into boric acid and hydrated chromium sesquioxide, potassium borate also remaining in solution. The precipitate is well washed, dried, and finely ground. It usually contains boric acid even after thorough washing. The washings and mother liquors are evaporated for the recovery of the boric acid.

According to the Chem. Zeit. 9, 851, the process now used on the large scale is as follows : The boric acid is first purified by solution in hot water, treated with animal charcoal, and recrystallised. The crystals are dried in a centrifugal machine. The mother liquor may be employed three or four times for recrystallisation of fresh portions of acid, but becomes then too impure for further use. Eight parts of potassium dichromate and 3 parts of purified boric acid are ground into a stiff paste with water, and the mixture in charges of about 1 cwt. is heated

to dull redness for about 4 hours in a reverberatory furnace. The fused mass is thrown into water, and washed repeatedly by decantation ; the pigment is ground while wet, again washed, filtered, and dried. The first two washings contain considerable quantities of potassium borate, which is recovered by evaporating in leaden pans, adding hydrochloric acid and allowing the boric acid formed to crystallise. The mother liquor is further evaporated and crystallised. The crystals are redissolved, the lead (from the pans) precipitated by hydrogen sulphide, and the filtrate recrystallised. In this manner, from 70 to 75 p.c. of the boric acid is recovered.

Guignet's green is the most permanent green pigment known ; it is unacted upon by light or concentrated boiling alkalis ; it is not affected by acids in the cold, but hot hydrochloric acid slowly dissolves it. When heated to 200° it becomes anhydrous. It is a fine green pigment largely used for the same purposes as the ordinary oxide. It may be used in place of the dangerous arsenical greens. It possesses good covering power, and can be mixed with other pigments without alteration. When mixed with lead chromate, it is employed for the production of a pale-green colour in landscape painting.

Other *chrome greens* are obtained by the use of sodium phosphate. These always contain some phosphoric acid. They are, however, not as brilliant as the oxide chrome greens. Various methods of preparation are employed. Arnaudon dissolves ammonium phosphate with slight excess of potassium dichromate in a little boiling water, evaporates until mass solidifies on cooling, heats at 80° and later at 200°, washes with hot water, dries and powders. Another method consists in boiling a solution of 10 lbs. potassium dichromate with 18 lbs. sodium phosphate, adding 10 lbs. sodium thiosulphate and a little hydrochloric acid, and boiling until precipitation is complete. The precipitate is washed, ground, and dried.

According to Bong (Ber. 29, 201), a blue pigment, retaining its colour at high temperatures, suitable for colouring porcelain, &c., is produced by igniting strongly, in the air, an intimate mixture of 5 parts boric acid, 15 parts alumina, 20 parts magnesium carbonate, and 2 parts barium chormate.

Chromyl dichloride CrO_2Cl_2. Moissan (Compt. rend. 98, 1581) prepared chromyl chloride by treating dry chromic anhydride with hydrochloric acid gas. It forms at the ordinary temperature but the action is accelerated by heating. It may also be made by distilling potassium bichromate (3 parts), common salt (3 parts) with sulphuric acid (9 parts) in an atmosphere of carbon-dioxide. The corresponding bromide and iodide cannot be made by this method, but the fluoride can, the formula for the latter being CrO_2F_2 (Gazz. chim. ital. 16, 218). Low and Perkin (Chem. Soc. Trans. 1907, 191) found that the best way of preparing this compound is to dissolve chromic anhydride (50 grams) in strong hydrochloric acid (170 c.c.) to which is added 100 c.c. of strong sulphuric acid, 20 c.c. at a time. Chromyl chloride sinks as a red liquid and may be separated in a tap funnel. B.p. at 760 mm. is 116·63° m.p. −96·5°, ±0·5°. It is a deep red liquid resembling bromine, D_4^{-47} 2·0528–2·0515, D_4^0 1·9501–1·9582, D_4^{15} 1·9124–1·9113.

Its vapour is not dissociated at 181° C. When heated in a closed tube to 180°-190° trichromyl chloride $(CrO_2)_3Cl_2$ is formed. It is a black non-crystalline powder deliquescing in air. Chromyl dichloride combines with phosphorus trichloride in carbon tetrachloride solution to form $CrOCl.POCl_3$.

Chromic chloride $CrCl_3$ or Cr_2Cl_6. The anhydrous chloride is obtained by heating a mixture of carbon and chromium sesquioxide in a current of chlorine. It can be also conveniently prepared by Burion's method (Compt. rend. 148, 170) by passing the vapour of sulphur chloride, b.p. 137–90, over the oxide gradually raised to a red heat. It forms pale-violet scales of sp.gr. 3 03 ; it is almost insoluble in water, but dissolves readily, being transformed to the green variety (v. infra), if only a minute trace of chromous chloride (1 in 20,000) is present. Chromic chloride may be prepared in solution by dissolving the hydroxide in hydrochloric acid. It forms two isomorphous hexahydrated salts $(CrCl_3,6H_2O)$, one blue and the other green, and also a tetrahydrate and a decahydrate. The blue hexahydrate, when dissolved in water, appears to give the ions $[Cr(OH_2)_6]'''$ and $3Cl'$, all the chlorine being precipitated by silver nitrate ; the green salt, however, at first forms the ions $[Cr(OH_2)_4Cl_2,2H_2O]$ and Cl', only $\frac{1}{3}$ its chlorine being immediately precipitated (Werner and Gubser, Ber. 1901, 34, 1579). In calico-printing a neutral solution of chromic chloride, prepared from potassium dichromate, is frequently used. The following method is recommended by De Karrur : Dissolve 9 lbs. of potassium dichromate in 5 gallons of boiling water. Prepare also a solution of 9 to 11 lbs. of white arsenic in 24 gallons of boiling water, and mix, with constant stirring, with the solution of dichromate. A greenish precipitate of chromic hydroxide soon separates ; it is cooled, filtered, and washed with boiling water. The precipitate is added in portions to a solution of hydrochloric acid (diluted until it no longer fumes), with constant stirring, until a portion remains undissolved. A solution of soda is then added and well mixed, until the hydroxide begins to precipitate. The dark-green solution, being thus neutralised, is evaporated to 46° B. and is ready for use. A basic chloride $CrCl(OH)_2$ is also employed as a mordant for silk and cotton.

Chromic fluoride $CrF_3,4H_2O$. This product is used in the printing and dyeing of woollen goods. It is a fine crystalline green powder, very soluble in water. It has a corroding action on glass, and is therefore best kept in lead or wooden vessels. It may be used as a mordant with both vegetable and animal fabrics, and is often employed in the place of acetate or nitrate of chromium for printing, and in general gives finer results. Alizarin dyes, cœrulein, gallein, &c., and logwood extracts, are fixed as perfectly as with acetate of chromium. One advantage in using it is that it is solid. It has no injurious effect on the pile, and is often used in place of chromates where the oxidising action of these is injurious, especially with wools. *Chromium silicofluoride*, prepared by dissolving the oxide in hydrofluosilicic acid, has also been used in dyeing and printing in place of the fluoride, and is stated to give better results.

Chromium nitrate. By dissolving strongly heated chromic oxide in hot concentrated nitric acid of D. 1·4 a solution is obtained from which the hydrate $Cr_2(NO_3)_6,15H_2O$ crystallises on cooling in the form of dark brown prisms $[a:b:c=1·4250 : 1:1·1158, \beta=93° 10']$. In contact with dry air the crystals lose $6H_2O$ with the formation of the grey coloured hydrate $Cr_2(NO_3)_6,9H_2O$ (Monatsh. 33, 9).

Chromium phosphate, formed by mixing cold solutions of chromic alum and disodium hydrogen phosphate, is a violet amorphous solid, which in contact with water becomes crystalline and has the composition $CrPO_4,6H_2O$. On boiling with water it is converted into the green crystalline hydrate $CrPO_4,4H_2O$. On further heating it loses two molecules and is converted into the dihydrate. When heated to low redness the phosphate becomes anhydrous and forms a black powder (Joseph & Rao, Chem. Soc. Trans. 1917, 111, 196).

Chromium phosphides. When finely divided chromium, prepared from amalgam, is heated with red phosphorus in a sealed exhausted tube the phosphide Cr_2P_3 is obtained. This on heating in hydrogen to 440° is converted to CrP. Both phosphides are grey and insoluble in acids.

Chromium arsenides. When finely divided chromium is heated with an excess of arsenic in a sealed exhausted tube, the product powdered and again heated, the grey arsenide Cr_2As_3,D_4^{22} 6·2 is obtained. When heated in hydrogen at 480°–500° a second arsenide CrAs is obtained D_4^{16} 6 35. Both compounds are insoluble in acids. (Zeitsch. anorg. Chem. 86, 291.)

Chromium sulphates. These are prepared by the solution of the hydroxide in sulphuric acid. It yields a bluish-violet solution, which, on boiling, becomes green. The experiments of Recoura have shown that numbers of compounds of different constitution exist both in the violet and green varieties, but they are not of commercial interest. Cf. Colson, Compt. rend. 1907, 144, 79, 206 ; Sénéchal, ibid. 1914, 159, 243. The double sulphates of chromium and potassium, sodium and ammonium, are, however, of importance. These are known as *chrome alums* ; they crystallise in fine octahedral crystals containing 24 molecules of water isomorphous with those of ordinary alum, and of corresponding composition.

Potassium chrome alum, *Chrome alum*

$$Cr_2(SO_4)_3 \cdot K_2SO_4,24H_2O$$

This substance may be prepared by mixing solutions of chromic sulphate and potassium sulphate in molecular proportions, or more conveniently by the reduction of potassium dichromate in sulphuric acid solution.

The best method is to add 5 parts of strong sulphuric acid to a solution of 3 parts potassium dichromate in 30 parts of water with the addition of a reducing agent, preferably a current of sulphur dioxide :

$$K_2Cr_2O_7+H_2SO_4+3SO_2+24H_2O$$
$$=K_2SO_4 \cdot Cr_2(SO_4)_3,24H_2O+F$$
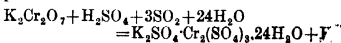
When the sulphur dioxide is substitute other reducing agents, such as alcohol, a quantity of sulphuric acid is required.

Chrome alum is obtained in large quantity as a by-product from the oxidation of substances by a mixture of p

dichromate and sulphuric acid, as in the oxidation of anthracene to alizarin, in the manufacture of aniline violet, &c.

Pure crystallisable violet chrome alum is prepared by the electrolysis of a solution of potassium dichromate mixed with sulphuric acid. The liquor is circulated in the cathode compartment which is separated from the anode by a porous vessel. The cathode is preferably of carbon. Dilute sulphuric acid is circulated in the anode compartment and the anode may be copper with copper turnings to utilise the SO_4 ions. (Inter. Cong. 1912.)

It crystallises in fine dark-purple octahedra, especially in presence of excess of acid, is soluble in 7 parts of cold water, forming a reddish-blue solution, which, when heated to about 70°, becomes green. It returns to its original colour after standing some weeks.

When heated to 25°–30°, the crystals lose half their water and become lilac-coloured; at 100° a further quantity of water escapes and the crystals turn green; at 350° they become anhydrous, but are still soluble in water; at a temperature slightly above 350° they become greenish-yellow, insoluble in water (Lowe), and only slowly soluble in acids. The green salt only contains ⅓ of the SO_4 as an acid ion, and is probably a sulphate of a sulphochromyl hydroxide. For these compounds, reference should be made to the extensive researches of Recoura (Ann. Chim Phys [7], 4, 494).

Chrome alum is used in dyeing, calico printing, and tanning.

Sodium chromealum $Na_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ corresponds to the potassium salt, but is more soluble in water.

Ammonium chrome alum

$$(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$$
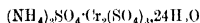
is prepared like the preceding alums It is less soluble in water than potassium chrome alum. It melts at 100°.

Chromium chlorate $Cr_2(ClO_3)_3$ is used to some extent in calico printing (Despierres and others, Dingl. poly. J. 228, 260–263), and for increasing the permanence of aniline black. It may be prepared by the addition of a solution of potassium chlorate to chrome alum or by the addition of barium chlorate to a solution of chromium sulphate, the barium sulphate being precipitated. According to Lauber and Weinreb (Dingl. poly. J. 257, 290), it is best prepared by the following process : Dissolve 60 parts of me alum in 80 parts (by weight) of hot r; add 20 parts of soda dissolved in 60 of water, and wash the precipitated hydrate. Redissolve the precipitate in 10 parts sulphuric acid of 66°B., filter if necessary 12 parts of potassium chlorate dissolved s of water. The solution is evaporated and the potassium sulphate crystallises more soluble chromium chlorate lution. When heated at 100° it quantities of chlorine and forms a d containing chromic acid and

chlorate is obtained by dissolving oxide in perchloric acid and tion. It forms short green and is very soluble in him. 1913, 103). Two

perchlorates are known $[Cr(H_2O)_6](ClO_4)_3$ and $[Cr(H_2O)_6](ClO_4)_3 \cdot 3H_2O$. Both salts are green. No sodium-chromi-perchlorate exists.

Chromic anhydride, *Chromic acid* CrO_3. This important oxide is best prepared by the decomposition of a chromate by sulphuric acid. A cold saturated solution of potassium chromate is added to from 1 to 1½ parts of concentrated sulphuric acid, with constant stirring. On cooling, if the acid used be strong enough, crimson crystals of chromic anhydride separate ; if necessary, the solution is evaporated until the crystals are formed on cooling. The liquid is poured off and the crystals drained on porous tiles or pressed between porous plates. They may be recrystallised by dissolving in water and evaporating to a syrup. The excess of sulphuric acid may be removed by the cautious addition of barium chromate to the solution of the crystals, or the crystals may be gently fused, when the heavier oxide sinks to the bottom of the vessel and the sulphuric acid above slowly evaporates. The mother liquors from the chromic anhydride are used for a fresh preparation until the percentage of potassium sulphate becomes excessive; they are then precipitated by the addition of lead acetate with the production of a light-coloured ' chrome yellow ' containing much lead sulphate.

According to Zettnow (Pogg. Ann. 143, 468), the largest yield is obtained as follows : 300 grams of potassium dichromate are dissolved in 500 c.c. of water, and 400 c c. of strong sulphuric acid are added. The mixture is allowed to stand for 10 or 12 hours, the solution decanted from the deposited crystals of potassium sulphate, and heated to 80° or 90° ; 150 c.c. of sulphuric acid are then added, followed by sufficient water to redissolve the chromic anhydride at first deposited, and the solution evaporated until the oxide commences to crystallise. The mixture is allowed to stand for 12 hours, decanted from the crystals, and evaporated with the production of a second and third crop of crystals. The crystals are drained, introduced into a crucible, mixed thoroughly with 50 c.c. of nitric acid of not less than 1·46 sp.gr. (weaker acid would dissolve the crystals) and drained for some hours on a tile. The operation is repeated if necessary with 25 c.c. of nitric acid. The whole of the sulphuric acid and sulphate having been thus removed, the crystals are heated on a sand-bath and the·nitric acid evaporated, or they may be heated to 80° in a current of air. In this manner, Zettnow obtained from 85 to 90 p.c.· of the theoretical yield of pure dry chromic anhydride.

Duvilliers (Compt. rend. 75, 711) prepares this oxide by dissolving 100 parts of barium chromate in 100 parts of water and 140 parts of nitric acid of sp.gr. 1·38 (40°B.) and heating the solution until it becomes red. 200 parts of water are then added, and the whole boiled for 10 minutes ; cooled, and the barium nitrate allowed to crystallise out. The solution is decanted, evaporated to the bulk occupied by the original amount of acid used, and a further crop of crystals of barium nitrate removed. The solution, which contains only about 1 part of barium nitrate for 200 parts of the anhydride, is evaporated nearly to dryness, a little water added, and the evaporation repeated until all the nitric acid is driven off. The anhydride is then crystallised out and dried as usual.

Barium chromate is digested for some time with about half the amount of dilute sulphuric acid required for complete precipitation, with the production of chromic anhydride and barium dichromate and precipitation of barium sulphate. Sufficient sulphuric acid is then added to just precipitate the barium, and the solution, which only contains chromic anhydride, is decanted from the precipitate and the solution evaporated (Meissner). According to C. Watts, the barium chromate is best treated with excess of strong nitric acid, the precipitated chromic oxide filtered through asbestos, and the nitric acid driven off by heat.

Chromic anhydride is a powerfully acid substance crystallising in scarlet rhombic prismatic needles of sp.gr. 2 788 (Zettnow) They melt at 193° without decomposition, and the melted mass exhibits supercooling ; at higher temperatures oxygen is evolved together with red vapours, probably CrO_3.

When heated to 250° they decompose into chromium chromate $CrO_3 \cdot Cr_2O_3 (=3CrO_2,$ also known as chromium dioxide) with evolution of oxygen Above that temperature, the whole is converted into chromium sesquioxide The perfectly dry anhydride, when heated to 120° *in vacuó*, slowly volatilises and condenses in red needles (Arctowski). By the action of light on a solution of this oxide, oxygen is evolved and chromium chromate precipitated as a brown powder.

Chromic anhydride is very soluble in water. 100 parts of water, at 26°, dissolve 62 parts of the oxide The aqueous solution contains Cr_2O_7'' ions, with a small proportion of CrO_4'' ions. These ions are capable of transformation by the action of acids or alkalis, as indicated by the equations :

$$(1) \ Cr_2O_7'' + 2HO' \rightleftarrows 2CrO'' + H_2O$$
$$(2) \ 2CrO_4'' + 2H \rightleftarrows Cr_2O_7'' + H_2O$$
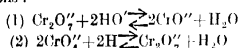
Datta & Dhar (J. Amer. Chem Soc. 1916, 38, 1303), from a study of the molecular solution volumes and molecular refractivities of chromic acid, potassium chromate and potassium dichromate, conclude that the formula of chromic acid is $H_2Cr_2O_7$ and not H_2CrO_4.

It dissolves in acetic acid or ether without decomposition ; is almost insoluble in sulphuric acid of 1·77 sp.gr , but dissolves in stronger or weaker acid ; is insoluble in nitric acid of sp gr. 1·46.

Chromic anhydride is a powerful oxidising agent. Warm anhydrous alcohol inflames when dropped upon it, and even dry ammonia gas is oxidised with production of water and nitrogen. Addition of oxalic acid is said to increase its oxidising power. The solution in water, sulphuric acid, or acetic acid, is largely used as an oxidising agent in organic work. In most of these oxidations, precautions must be taken to moderate the velocity of the reaction. When acetic acid is used as the solvent, the substance to be oxidised is usually dissolved in the same solvent and the oxidising solution slowly added, the temperature being kept sufficiently low, *i.e.* seldom above 100°. Chromic acid, as an oxidising agent, has the advantage that the close of the reaction is frequently indicated by a pure green colour in place of the brownish colour.

It has the property of producing a permanent yellow colour with silk or wool, but not

with cotton. The chromium in such material may be converted into lead chromate upon the fibre or further dyed by logwood, &c. Chromic anhydride usually contains sulphuric acid and sulphates or nitrates ; Moissan found 24 p.c. of sulphuric acid in samples of the commercial article.

Chromates. All chromates are prepared, directly or indirectly, by the action of oxidising agents upon *chrome iron ore* or *chromite* FeO· Cr_2O_3. This important mineral is widely distributed and extensively mined. Large deposits are found in New Caledonia, containing sometimes 5 p.c. of chromium sesquioxide in a form soluble in acid, probably as chrome ochre.

Chromite belongs to the spinel group of minerals. It is isomorphous with magnetic iron ore $FeO \cdot Fe_2O_3$, and may be considered as that substance in which the sesquioxide of iron is replaced by sesquioxide of chromium. A portion of the chromium is usually replaced by aluminium, and some of the iron by magnesium, though this is sometimes absent. The composition of chromite varies extremely ; an ore, containing 50 p.c of the sesquioxide, is of very good quality. Of seven samples from varying localities analysed by Clouet, the chromium sesquioxide present averaged 44 p.c. For analyses *v.* CHROMITE. Chromite is black or brownish-black, and infusible before the blowpipe. It will scratch glass, but is itself scratched by a good steel knife.

A scheme for the analysis of chromite has been given under the estimation of chromium.

The chief use of chromite is as a refractory lining in steel or copper furnaces. Smaller amounts are employed in the manufacture of chrome-steel alloys and of chromium compounds.

Potassium chromates. Both the normal and acid chromates are of importance in the arts. The acid or dichromate, containing the larger proportions of the active constituent CrO_3, is generally prepared on the large scale.

A great number of processes have been adopted for the treatment of chromite for this purpose; they all depend upon the oxidation of the chromium sesquioxide into chromic anhydride.

The ore is heated to redness and plunged into cold water to facilitate the powdering, stamped, ground in a mill, and finely sifted.

In former times, the ore was mixed with about two-fifths of its weight of potassium nitrate and ignited on the bed of a reverberatory furnace, the oxygen required for the oxidation of the sesquioxide into the anhydride and the potassium for its conversion into potassium chromate, being both provided by the nitrate. A great saving was introduced by the substitution of atmospheric oxygen as the oxidising agent in place of the nitre, the potassium being supplied by potassium carbonate or, as proposed by Watt, by potassium sulphate. The latter salt is largely used where, as in Russia, the demand for potassium sulphate is small, and hence this salt, produced during the later conversion of the chromate to dichromate, is used to replace some of the potassium carbonate. The mass, however, we very liable to fuse and the heavy particles chromite to sink through the liquid and escape the action of the blast. This difficulty overcome by Stromeyer, who introduced l into the mixture, thus rendering the mass por and non-fusible and much increasing the rap and completeness of the action.

Tilghmann (Patent 1847) makes use of felspar as the source of alkali. For this purpose, 1 part of chrome ore is mixed with 4 parts of felspar and 4 parts of lime or 7 parts of chalk. The mixture is heated to bright redness, but not to fusion, in a reverberatory furnace for about 20 hours, with constant stirring. The chromate thus produced is removed as described later.

The ore may also be mixed with potassium chloride, and heated to whiteness with frequent stirring while a current of superheated steam is passed over the mass ; the iron is stated to pass away almost entirely as chloride (Swindells, Chem. Gazz. 1851, 419).

Jacquelain (Ann. Chim. Phys. [3] 21, 478) prefers to produce calcium chromate in the furnace and to convert it subsequently into the required chromate by double decomposition. He thus avoids the loss of alkali always experienced in the ordinary process. The ore is *finely powdered*, preferably levigated and dried before use, mixed ultimately with chalk in the required proportions, and heated to bright red- ness on the bed of a reverberatory furnace for 9 or 10 hours, with occasional stirring (at least once an hour). The product is ground in a mill, suspended in hot water, and treated with sulphuric acid until slightly acid ; calcium dichromate is thus produced. A little chalk is stirred into the solution to precipitate the iron as oxide, and a solution of potassium carbonate or other salt, according to the chromate re- quired, is added. The calcium is thus precipi- tated as carbonate and the dichromate required remains in solution. The solution may also be used directly for the production of chrome yellow, &c.

According to Booth's method (Pat. 1852, Dingl poly J 131, 137), the ore is mixed with one-fifth of its weight of charcoal or coal and ignited in a reverberatory furnace like that used for puddling iron, out of contact with the air The product is thrown into vats, and the reduced iron dissolved out by dilute sulphuric acid, the residue being treated in the usual manner for the production of chromates. The weight of oil of vitriol used, amounts to about two-thirds that of the ore. It is stated that the value of the ferrous sulphate obtained repays the extra labour involved.

Atcherley (Hoffman's Ber. u Entw. Chem. Ind. [1] 725) gives a description of the manu- facture of potassium dichromate as usually practised on the large scale, of which the follow- ing is an abstract :—

The ore is stamped, ground in a mill, and passed through a sieve of 80 meshes to the inch.

Potash lye is prepared by soaking 7 cwts. of burned limestone (containing but little silica and magnesia) in a solution of 2¼ p.c. of potassium carbonate free from chloride (which would hinder the crystallisation of the product), dried, ignited, and powdered.

It is then mixed with 4½ cwts. of the ore, and spread in a layer 2 inches deep upon the pre- viously heated bed of a reverberatory furnace, at the end nearest the fire. The furnace is about 9 feet long and 6 feet broad. The heat is maintained at bright redness, and the mixture turned over every 15 minutes ; in about 2 hours it is gradually pushed towards the farther end

of the furnace, and its place supplied by a fresh charge. The operation is completed in about 4 hours, when the mass is greenish-yellow and contains chromates of potassium and calcium, lime, potassium silicate, and ferric oxide. It is broken into coarse powder and lixiviated in wooden pans, placed steplike one above another, with a hot solution of potassium sulphate, which converts the calcium chromate into potassium chromate with precipitation of calcium sulphate. The liquid is allowed to run from one vat to another, until at last a saturated solution of potassium chromate is produced. This is run into a depositing vat lined with lead and treated with sufficient sulphuric acid and water to con- vert the normal salt into the dichromate, and the solution cooled.

As the solution of normal chromate was saturated and contained about 1 part of salt in 2 parts of solution, the dichromate solution formed is supersaturated, that salt requiring nearly five times as much water for solution as the normal chromate ; about three-quarters of the total amount in solution is thus deposited on cooling. The crystals are redissolved in sufficient water to form a solution of 1·120 sp.gr. and crystallised in deep iron pans at a temperature of 21°.

The production of chromates is said to be rendered easier by the addition of oxygen- carriers, such as manganates or oxides of copper or iron (D. R. P. 163814). A method de- pendent on this, in which ferric oxide obtained by heating pyrites is used, is the following : 240 parts chrome iron ore of 50 p.c , 170 parts sodium carbonate, and 150 parts ferric oxide, with, if desired, 50 to 80 parts lime, are intimately mixed, roasted, and lixiviated. The residue contains all the original ferric oxide and may be used over again. The solution is concentrated and treated as usual. The action of the ferric oxide is regarded as due to the production of an alkaline ferrite which becomes converted to the chromate and ferric oxide (J. Soc. Chem. Ind. 1895, 865).

Chromates are also produced by mixing finely divided chrome iron ore with alkaline carbonates and roasting in an oxidising atmo- sphere in a revolving furnace at a temperature sufficient to keep the mass fluid (National Electro- lytic Co. New York ; J. Soc Chem. Ind. 1908).

Potassium chromate K_2CrO_4 is prepared, as already described, from chrome ore. It may be produced by adding potassium hydroxide to a solution of the dichromate. It crystallises in anhydrous yellow rhombic prisms isomor- phous with those of potassium sulphate, sp.gr. 2·71 (Kopp). 100 parts of water dissolve of potassium chromate

at	0°	30°	60°	105·8°
	54·57	65·13	74·6	88·8 parts,

105·8° being the boiling-point of the saturated solution. The solution has a fine yellow colour of great tinctorial power ; a distinct yellow tinge is imparted by 1 part in 400,000 parts of water. It is insoluble in alcohol and ether, and is very poisonous, producing a condition resembling diabetes when administered by mouth or sub- cutaneously. It also produces slow-healing sores, especially among workers in chromate factories. For these, a sodium bisulphite wash

is efficacious. Such workers should pay attention to constant washing of face, nose, and hands, and packers are advised to wear respirators.

When heated, it reddens and fuses without decomposition; heated with reducing agents, such as sulphur, it is reduced to chromium sesquioxide. The addition of an acid, even carbonic acid, determines the decomposition into potassium dichromate, as is indicated in the previous equations, and it is evident further that, even when excess of acid is present, the solution still contains CrO_4'' ions The equations also indicate that a solution of potassium chromate possesses an alkaline reaction

$$2CrO_4'' + H_2O \leftrightharpoons Cr_2O_7'' + 2HO'$$
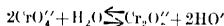
Owing to the much smaller solubility of the dichromate (4 64 parts at 0°), when the chromate is crystallised some dichromate also separates

It forms double salts with the chromates of the alkaline earths and lead.

Potassium chromate is not largely used, the dichromate, on account of its greater richness in chromic acid, being generally preferred. The general uses and oxidising properties, however, described under potassium dichromate, also apply to the normal chromate

Potassium dichromate, generally known as ' Bichromate,' or ' Bichromic,' $K_2Cr_2O_7$. This important salt is prepared in large quantities by the methods already described. It may be made electrolytically by the use of a solution of potassium hydroxide, a cathode of porous copper oxide, and an anode of ferrochrome (50 p c), which has an E M F. of 2 volts . ferric oxide is also formed and precipitated (Lorenz, Zeitsch. anorg. Chem 1896, 12, 396). Considerably over 10,000 tons are annually produced in Great Britain.

It crystallises in anhydrous, fine, red, square tables, derived from triclinic prisms, of sp gr. 2·692, and of intensely metallic, bitter taste. They melt at about 400° (Tilden and Shenstone), and resolidify on cooling without change. At bright redness, decomposition ensues, and the normal chromate and chromic sesquioxide result. Other chromates of composition, $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$, appear to exist in equilibrium with the solution with certain limits of concentration.

100 parts of water dissolve at 0°, 4·64 parts ; at 30°, 18·13 parts ; at 60°, 45·44 parts : and at 104·8°, 108·2 parts ; 104·8° being the boiling-point of the saturated solution (Koppel and Blumenthal, l.c.).

Potassium dichromate is used in the preparation of all chrome pigments ; of ' discharge ' for Turkey red, &c. ; for the production of a large variety of colours in calico printing and dyeing ; in the manufacture of safety matches, &c. In solution with sulphuric acid, it is used as a bleaching agent for tallow, palm oil, &c. ; in the oxidation of anthracene to alizarin, and in the manufacture of aniline violet and in many other organic oxidations. It is also used for tanning leather (v. LEATHER).

When mixed with organic substances it is reduced on exposure to light ; gelatine under such circumstances is rendered insoluble. This reaction is taken advantage of in the ' Carbon ' process of photography. The gelatine is mixed with a pigment of any colour,

and the paper carrying this film is sensitised by floating on a solution of potassium dichromate. On exposure under a negative, the gelatine in those portions exposed to the light becomes insoluble, and retains the pigment, while the portions protected by the darker parts of the negative are almost unacted upon, and may be dissolved in warm water. In this manner, photographs of any desired colour, and of great beauty and permanence, may be produced. Contact of the chromated gelatine with the reduced silver of an ordinary bromide print has a similar effect, and bromide photographs may hence be copied by squeezing into contact with a sensitised pigmented gelatine. After a few minutes' contact, the pigmented paper is developed like a carbon print. The bromide has become bleached and reduced to silver, but can be redeveloped. The insoluble gelatine does not absorb water, but will take oil, which may be mixed with any desired pigment, and this forms the basis of the oil and bromoil processes. Gum, mixed with dichromate, is also made insoluble by exposure to light, and this is made use of in photography in the gum dichromate process (v. PHOTOGRAPHY.

Sodium chromates. The normal chromate $Na_2CrO_4, 10H_2O$ and the dichromate $Na_2Cr_2O_7$, $2H_2O$ are prepared by methods corresponding to those used for the potassium salts   According to Nic. Walberg (Dingl poly J 259, 188), they are prepared on the large scale as follows: 6 parts of powdered chrome ore (44 p c. Cr_2O_3) are mixed with 3 parts soda ash (92 p.c. Na_2CO_3) and 3 parts of chalk, and heated in charges of 1 ton in a reverberatory furnace for 8 hours. The mass is lixiviated to produce a solution of 45°B , boiled down to 52°B , and allowed to crystallise in leaden pans The crystals are first dried by a centrifugal machine, and finally heated to 30° in a drying chamber, where they crumble to a yellow anhydrous powder containing about 96 p c of the normal chromate.

For the production of dichromate, these crystals are dissolved to a solution of 40°B. and treated with sufficient chamber acid to determine the conversion into the dichromate, the right point being found by potassium iodide and starch paper. Sufficient neutral sodium chromate is then added to bring the percentage of CrO_3 to about 72·5. The liquor is cooled in lead tanks to 1°, artificially if necessary, and the sodium sulphate crystallised out. The liquor is drained off, filtered if necessary, and evaporated to dryness in an iron pot, with constant stirring. The residue is powdered while still hot. If the amount of CrO_3 be allowed to exceed 72·5 p.c., the product is damp and cannot be stored in wooden casks   An analysis of this substance showed CrO_3, 72·3 ; Na_2O, 26·20 ; SO_3, 1·40.

Newer methods of manufacture are the treatment of the monochromate with ammonia, followed by carbonation and deposition of sodium bicarbonate ; the use of caustic alkali in the place of alkali carbonate ; and the employment of only half the necessary sodium carbonate required to decompose the ore, the remainder being replaced by sodium sulphate, formed in the later stages of manufacture (Ulm, Chem. Zeit. 1914, 38, 670 ; J. Soc. Chem. Ind. 1914, 33, 917).

Normal sodium chromate forms fine large efflorescent crystals of the composition

$$Na_2CrO_4,10H_2O$$
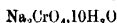
isomorphous with Glauber's salt. Unlike potassium chromate, it is less soluble than the dichromate; it is, however, more soluble than potassium chromate, 100 parts of water at 30° dissolving 87·36 parts of sodium chromate.

Other hydrates with 6 and 4 mols. of H_2O are known. Their transition temperatures have been suggested as convenient fixed points in thermometry. (Richards & Kelley, J. Amer. Chem. Soc. 1911, 33, 847.)

Sodium dichromate $Na_2Cr_2O_7,2H_2O$ crystallises in thin, six sided prisms with bevelled edges of a fine hyacinth-red colour, and is very soluble in water, 100 parts of water at 30° dissolving 197·6 parts of the salt. It is hence more than 10 times as soluble as potassium dichromate, which frequently makes its use preferable to that of the potassium salt.

Ammonium chromate and **dichromate** are prepared by mixing in proper proportions solutions of ammonia and of chromic acid. The dichromate, on heating, yields nitrogen, water, and chromic oxide, and forms a convenient method for the preparation of nitrogen free from argon

Lead chromates. The *neutral lead chromate* $PbCrO_4$ is best produced by the action of a solution of lead acetate on a solution of a chromate. Thus produced, it is of a fine lemon-yellow colour, insoluble in water and dilute acids. When heated at 250°, it becomes reddish-brown, at a higher temperature it fuses, and finally evolves oxygen with the formation of chromic sesquioxide and a basic lead chromate. On account of this evolution of oxygen on heating, this substance is frequently used in organic analysis.

Lead chromate is soluble in cold lime water or caustic alkali, but is unattacked by hot lime water. For this reason, in immersing calico coloured with chrome yellow in lime water, for the production of an orange colour, care should be taken that the solution is hot.

When heated with caustic alkali, a portion of the chromic oxide is removed, with the production of a basic lead chromate of colour varying from orange to vermilion.

The *normal chromate* is largely used as a pigment, and for calico printing, and is the essential constituent of various chrome pigments as *Chrome yellow, Paris yellow, Leipsic yellow.* The name *Cologne yellow* was originally given to chrome yellow containing a mixture of lead chromate and lead sulphate, but the latter compound is usually present in pale yellows known commercially as ' pure ' chrome yellows.

Chrome yellows. The finest chrome yellow is produced by precipitation; the lead acetate used should not be basic, or the product will be of an orange colour; the solution should be dilute, and the lead salt should be in excess; the presence of excess of chromate is liable to ' turn ' the yellow—*i.e.* to produce an orange tinge. The substances used should be comparatively pure.

For the lighter yellows, the solution of chromate is mixed with an appropriate quantity of sulphuric acid, Glauber's salts or alum (American chrome yellow), before precipitation;

the latter yields good colours but considerable care is required in the precipitation. The lead chromate is thus precipitated, together with any desired amount of sulphate, and the colour correspondingly lowered. For cheaper chromes, the colour is toned down by the admixture of kaolin, barytes, gypsum or whiting, the finely powdered solid being ground with water and well mixed with water in the tank into which the precipitating liquids are run (*vide infra*). Bouthron Chatard gives the composition of ordinary Cologne yellow as $CaSO_4$, 60 p.c.; $PbSO_4$, 15 p.c : $PbCrO_4$, 25 p.c.

Biot and Debise first precipitate lead sulphate from a solution of the acetate, and digest 3 parts of the washed precipitate with 1 part of normal potassium chromate dissolved in hot water. The chromate is thus wholly converted into chrome yellow, mixed or perhaps combined with the lead sulphate, and a ' Cologne yellow ' of good colour is produced. The colour is said to be equal to that obtained when double the quantity of chromate has been used. Its covering power is, however, stated to be inferior to that of the precipitated yellow.

Milbauer & Kohn (Zeitsch. physikal Chem. 1916, 91, 410) show that the reaction $PbSO_4 + K_2SO_4 \rightleftharpoons PbCrO_4 + K_2SO_4$ proceeds practically completely in the direction of left to right. From determination of the stability it is shown that the solid phase $PbSO_4$ cannot exist in the presence of $K_2CrO_4K_2SO_4,PbCrO_4$, and that the existence of double salts is unlikely. The general results show that the manufacture of chrome yellows can be carried out from lead sulphate and that various shades can be obtained by varying conditions, temperature, concentration and time. It follows also that an excess of lead acetate should be used in the manufacture since this will secure the absence of K_2CrO_4 which would otherwise rapidly convert the lead sulphate necessary for the particular shade into chromate.

Liebig uses for this purpose the lead sulphate obtained in dye works, &c., as a by-product. The pigment, on account of the basic character of the sulphate, is of an orange colour.

Anthon substitutes lead chloride for sulphate, treating 100 parts of freshly precipitated chloride with 27 parts of dichromate.

The method usually adopted for production of chrome yellow is the following : The two precipitating solutions are placed separately in wooden tanks, and heated by steam pipes. The solutions are either filtered or allowed to settle in the tanks and drawn off from above. They are run together into the precipitating tank, which contains about 200 gallons. The chrome yellow is allowed to settle and the clear liquid drawn off; more water is added, the whole thoroughly stirred and the process is repeated three or four times. The pigment is then put in a filter press and dried at as low a temperature as possible.

According to the Textile Colourist, the preparation of chrome yellow is as follows : For the preparation of the lead acetate, four wooden tubs, 3 feet in diameter and 1½ feet high, are arranged one above another, so that the liquid may pass downwards from one to the other. They are filled with granulated lead, and strong wood vinegar poured on the uppermost; after

remaining there for a few minutes, it is run into the second, third, and fourth for an equal time. The surface of the lead is thus thoroughly acted upon, and becomes heated and oxidised by the air. The vinegar is then passed through a second time, remaining in each tub for an hour; on leaving the fourth tub, a saturated solution of acetate is produced.

Bichrome is dissolved in 10 or 12 parts of water in steam-cased copper pans, and sufficient acetate added to just precipitate the chromate completely. The precipitate is settled, washed by decantation, filtered, and dried slowly on boards. The filtration should be performed as rapidly as possible, because the pigment swells considerably while drying, and this should take place on the boards.

By mixing some lead chromate with the lead acetate solution, a dark lemon colour is produced, and by the addition of caustic potash to the precipitate, a much redder pigment may be obtained.

The chrome yellows, by mixture with Prussian blue, form greens known as 'Brunswick greens' and also as 'chrome greens' (not the true *chrome green, vide supra*). These are valuable and cheap pigments, but not as stable as the corresponding *zinc greens (vide infra)*.

By removal of some of the acid from normal lead chromate, a *basic* lead chromate of a deep red colour is obtained, $PbO \cdot PbCrO_4$, which is the base of a number of *chrome reds*. Between these and the various yellows a large number of shades of *chrome orange* may be obtained. The chrome reds are known by a variety of names, *e.g.* Austrian cinnabar, Persian red, Chinese red, Victoria red, Derby red, American vermilion, &c.

The pigment is usually prepared by boiling chrome yellow with caustic alkali or by boiling together the lead salt, potassium dichromate, and an alkali. One such method is—20 parts of white lead are mixed into a fine paste with water, 10 parts of potassium dichromate and 3 of caustic soda, are dissolved in a little water, added, and the whole boiled until the desired colour is obtained. It is then washed and dried.

Runge mixes 45 parts of litharge, 6 parts of salt, and 50 parts of water; the mass becomes white, and swells considerably; more water is added to prevent it from hardening. In three or four days, the whole has been converted into lead oxychloride; a solution of 15 parts of potassium dichromate is then poured on, and the mass well stirred and washed. A corresponding process is used with carbonate of lead, the colour produced being preferable to that when chloride, sulphate, or oxide of lead are used.

For the production of a fine 'Persian red,' Prinvolt digests 25 parts of lead carbonate in a cold solution of 10 parts of potassium chromate for 2 days. A red crystalline precipitate of basic lead chromate is thus produced, while potassium bicarbonate remains in solution. The mixture is boiled for half an hour, whereby a portion of the red precipitate becomes decomposed, with the formation of normal lead chromate and of potassium chromate, turning a violet-red colour. This is filtered off, washed, and digested with one part of sulphuric acid dissolved in 100 parts of water, with the production of 'Persian red.'

For the production of a fine vermilion pig-

ment, Liebig and Wöhler's method may be used. A mixture of equal parts of potassium and sodium nitrates is just heated to fusion, and chrome yellow, in small fragments, is dropped in; ebullition takes place, and the mass becomes black. The heating should be continued until ebullition ceases. The chrome yellow has thus become converted into basic lead chromate and potassium chromate. If the temperature used be too high, the product becomes brown and is spoiled. The supernatant yellow liquid is poured from the heavy basic lead salt, which is then well washed in water. The washings should be poured off as quickly as possible, or the action is liable to be reversed and the normal chromate reproduced in part, with a corresponding reduction of colour.

The colour of the varieties of chrome red is due principally to the size of the crystals, those pigments of which the crystals are largest being of the most intense colour.

For the production of *chrome orange*, the chrome yellow is boiled with lime or alkali (in smaller quantity than that used for production of chrome red), until the shade required results. The cheaper chrome orange pigments, as in the case of the yellows, contain admixed kaolin, gypsum, &c.

The lead chromates all possess good covering power and brightness of colour; they are durable, but blacken under the action of sulphuretted hydrogen. They mix well with other pigments, but should not be used with sulphides.

Calcium chromate $CaCrO_4, 4H_2O$ is largely produced in the manufacture of chromates from chrome iron ore. It is soluble in water and alcohol It becomes anhydrous at 200°, and is then almost insoluble in water.

Barium chromate $BaCrO_4$ is a canary-yellow powder, known as *Yellow ultramarine* or *Lemon yellow*. It is produced by the addition of a chromate to a solution of a salt of barium.

Barium chromate is insoluble in water and acetic acid, soluble in hydrochloric and nitric acids. On treatment with a boiling solution of chromium anhydride, it dissolves, and crystallises on cooling as a yellowish-red powder, consisting of the dichromate $BaCr_2O_7, 2H_2O$.

Both barium and calcium chromates have been employed as pigments, but are now little used on account of their lack of brightness and covering power.

Bismuth chromates. The addition of potassium dichromate to a neutral solution of bismuth nitrate gives a yellow flocculent precipitate, $3Bi_2O_3 \cdot 2CrO_3$, soluble in acids (Löwe). On heating, it becomes partly decomposed and turns greenish. From an *acid* solution of bismuth nitrate, the precipitate formed consists of $Bi_2O_3 \cdot 2CrO_3$ (Löwe; Muir), and is quite insoluble in water. Bismuth chromate is used as a pigment and in calico printing.

Zinc chromate, Zinc yellow, or **Buttercup yellow** $ZnCrO_4$, is a beautiful, stable, yellow pigment, produced by the addition of hot neutral solution of zinc sulphate to potassium chromate, or by adding a cream of zinc oxide in water to a boiling solution of potassium dichromate.

Zinc chromate can be obtained in various tints and has a good colour. Though not equal to *chrome yellow* in covering power or body, it

has the advantage of not blackening by exposure to sulphides. It is largely used for mixing with *Prussian blue* to form the *zinc greens*, which are more stable and faster to light than the corresponding *chrome greens*.

Perchromic acid. On adding hydrogen peroxide to an aqueous solution of chromic acid, or to an aqueous solution of a chromate acidified with sulphuric acid, a deep blue colouration is produced, which on shaking the solution with ether passes into that liquid. The colour of this substance is so intense that it constitutes a delicate test for both chromic acid and hydrogen peroxide. It is extremely unstable, evolves oxygen, and is gradually transformed into chromium trioxide. It has been regarded as $Cr_2O_7 \cdot xH_2O$ (Barreswil), $CrO_6 \cdot 3H_2O$ (Fairley), $CrO_3 \cdot H_2O_2$ (Moissan), and $2HCrO_4 \cdot H_2O_2$ (Berthelot). By adding pyridine, quinoline, and other organic bases to the ethereal solution of the blue compound, Wiede obtained salts of an acid he regarded as $HCrO_5$. He also obtained blue salts $(NH_4)CrO_5 \cdot H_2O_2$ and $KCrO_5 \cdot H_2O_2$ According to Riesenfeld (Ber. 1905, 38, 4068; 1908, 41, 2826; 1911, 44, 147), these salts are acid salts of *perchromic acid* H_3CrO_8, of the type MH_2CrO_8, corresponding with the red perchromates. Pure perchromic acid $H_3CrO_8 \cdot 2H_2O$ may be obtained by the interaction of chromic trioxide and 97 p.c. hydrogen peroxide in methyl ether solution at $-30°$:

$$2CrO_3 + 7H_2O_2 = 2H_3CrO_8 + 4H_2O$$
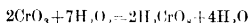
After the reaction is complete, the blue solution is poured off, dried with phosphoric oxide, and evaporated *in vacuo* at $-30°$. It forms a dark blue crystalline mass, which decomposes at above $-30°$. The water is regarded as water of constitution, since the blue colour is only produced in presence of water. The red perchromates are considered as the anhydro salts of the blue perchromic acid (Riesenfeld and Mau, Ber. 1914, 47, 548).

Esters of chromic acid have been prepared by Wienhaus (Ber. 1914, 47, 332) by shaking a tertiary alcohol, dissolved in light petroleum or carbon tetrachloride with an excess of solid chromium trioxide. The ester remains dissolved or suspended in the solvent, from which it can be obtained by evaporation.

CHROMAMMONIUM COMPOUNDS AND DERIVATIVES

Salts of chromium readily combine with ammonia or substituted ammonias, to form complex compounds in which the chromium atom may be combined with six molecules of ammonia, as, for example, in hexamine chromium chloride $[Cr(NH_3)_6]Cl_3$. According to Werner's theory, the chlorine of this compound is united by primary valencies, whereas the ammonia is co-ordinated with the chromium atom by supplementary valencies (Ber. 40, 20). The ammonia may be substituted by acid groups, the valency and character of the complex radical being determined by the acid and basic radicals in the molecule, as will be evident from the following description of some of the simpler compounds.

Hexamine chromium salts (luteo salts), e.g. the nitrate $[Cr(NH_3)_6](NO_3)_3$, are prepared by treating the corresponding purpureo salts with ammonia in cold concentrated solution (Jörgensen, J. pr. Chem. 23, 229; Mills, Phil. Mag. [4] 35, 245).

Pentamine chromium salts (purpureo salts). Jörgensen (J. pr. Chem. 2, 20, 105) prepared the chloride $[CrCl(NH_3)_5]Cl_2$ by reducing violet chromic chloride in a stream of pure dry hydrogen at a red heat, and adding to it a solution of NH_4Cl in strong ammonia. Air was passed through, HCl added, and the mixture boiled, when a carmine coloured powder is precipitated. It crystallises in octahedra, sp.gr. 1·687, dissolves in 154 parts of water at 16°. Representing the compound $Cl_2Cr_2(NH_3)_{10}Cl_4$, Jörgensen found that only 4 atoms of chlorine are precipitated by silver nitrate, which confirms Werner's formula above given.

Triamine chromium salts. These compounds have been investigated by Werner (Ber. 1910, 43, 2286), who uses triamine chromium tetroxide in their preparation. To a well-cooled solution of 30 grams of chromic acid in 300 c.c. of water are added 300 c.c. of pyridine. After remaining half an hour in a freezing mixture, 750 c.c. 3 p.c. H_2O_2 are added. The precipitated pyridine perchromate is collected, washed, and added to 90 c.c. of well-cooled 25 p.c. ammonia. The precipitated triamine chromium tetroxide is collected after 10 minutes and washed with water, alcohol, and ether.

Trichlorotriamine chromium $[(NH_3)_3CrCl_3]$ results when triamine chromium tetroxide is added to cold concentrated hydrochloric acid. A bluish-grey precipitate is formed, and the filtrate from this deposits the compound after standing two days, in dark blue crystals with a greenish tinge. The triaquo derivative

$$[Cr(OH_2)_3(NH_3)_3]Cl_3$$
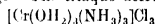
is obtained by treating one gram of the dichloro-aquotriamine chromium chloride (contained in the grey precipitate above mentioned) with 8 c.c of water covered with 5 c.c. of pyridine. The resulting solution is filtered, and the hydroxoiodide precipitated by the addition of solid potassium iodide. The chloride is obtained from this by triturating with hydrochloric acid. It forms brownish-red hygroscopic crystals. The corresponding bromine compounds have been prepared.

The diamine chromium compounds were among the earliest known of these complexes. Morland (Chem. Soc. Trans. 13, 252) obtained a compound by the action of $K_2Cr_2O_7$ on fused KCNS, which was subsequently examined by Reinecke (Annalen, 126, 113) and by Nordenskjold (Zeitsch. anorg. Chem. 1, 126), who prepared it by heating NH_4CNS to incipient fusion and dropping in one-third of its weight of $(NH_4)_2Cr_2O_7$. The compound

$$[Cr(NH_3)_2(SCN)_4]NH_4$$
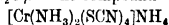
is known as Reinecke's salt, and according to Werner is the ammonium salt of tetrathiocyano-diamine chromite, the complex molecule having an acid character and being mono-valent. It forms small red crystals fairly stable towards acids. The potassium salt is obtained by adding KCl to its solution, and the acid $[Cr(NH_3)_2(SCN)_4]H$ by decomposing the barium salt with sulphuric acid. It commences to decompose at 80°. Werner and Klein (Ber. 35, 277), by oxidation of ' Reinecke's salt ' with bromine, completely

eliminated the four thiocyano groups with the formation of dibromodiaquodiamino chromic bromide $[(NH_3)_2CrBr_2(H_2O)_2]Br$.

The last member of the series in which all the ammonia groups are replaced by acid radicals may be represented by the salt $[Cr(CN_6)]K_3$ potassium chromcyanide or hexacyanochromite. It is obtained in light yellow monoclinic crystals by adding a solution of chromic acetate to a boiling solution of potassium cyanide.   G. S. B.

CHROMOCYANINES v. OXAZINE COLOURING MATTERS.

CHROMOFORM. Trade name for an orange-red crystalline powder formed by the union of dichromic acid and hexamethylenetetramine $(C_6H_{12}N_4(CH_2)_2Cr_2O_7$ Slightly soluble in alcohol and cold water, readily soluble in hot water The aqueous solution on boiling, or by treatment with acids or alkalis, evolves formaldehyde.

CHROMOGEN AND CHROMOPHORE v COLOUR AND CHEMICAL CONSTITUTION.

CHROMOMETERS v COLORIMETERS

CHROMONE. Colouring matters derived from chromone or pheno γ pyrone (1), the analogue of coumarin (2)

(1)   (2)
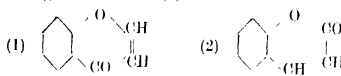
or pheno α pyrone, have not as yet been found in nature, though an hydroxy chromone (1) analogous to daphnetin (2) will no doubt possess dyeing properties and yield a yellow shade on aluminium mordant .

(1)   (2)
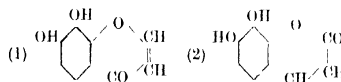
Chromone is specially interesting owing to the isolation of the 3 hydroxy-chromonol
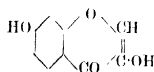
by Schall and Dralle (Ber. 1881, 21, 3009) as one of the products of the alkaline oxidation of brazilein. Benzo γ-pyrone derivatives were first synthesised by v Kostanecki (Ber. 1900, 1998), but the synthesis of chromone itself is due to Ruhemann and Stapleton (Chem Soc. Trans. 1900, 1179). When phenoxyfumaric acid (1) is treated with sulphuric acid benzo γ-pyrone carboxylic acid is produced (2) :

C_6H_5—O—C—COOH   → C_6H_4 C—COOH

HO·CO—CH

(1)   (2)
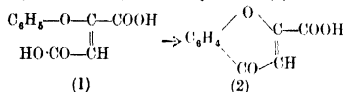
and this when heated in a vacuum yields benzo γ-pyrone :

C_6H_4
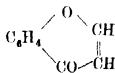
It crystallises in colourless needles, m.p. 59°,

and its yellow solution in cold sulphuric acid possesses a blue fluorescence.   A. G. P.

CHROMOTROPE or **CHROMOTROPIC ACID,** 1:8-Dihydroxynaphthalene-3:6-Disulphonic acid.

CHRYSANILINE. *Diamidophenylacridine* $C_{19}H_{15}N_3$, is obtained as a by-product in the manufacture of rosaniline by the arsenic acid method, and was isolated by Nicholson (Dingl. poly. J. 168, 133) by treating the residue with steam, whereby chrysaniline passes into solution and can be precipitated therefrom by addition of nitric acid It was further examined by Hofmann (Ber 1869, 378), who prepared its methyl-, ethyl-, and phenyl- derivatives, and showed that it possessed the empirical formula $C_{20}H_{17}N_3$ Its composition and constitution were first established by Fischer and Körner (Ber 1884, 203 . Annalen, 226, 175), who showed that a second lower homologue of composition $C_{19}H_{15}N_3$ was present (compare also Anschutz, Ber 1884, 433), and who refer its formation in the rosaniline melt to a condensation and subsequent oxidation of orthotoluidine and aniline, since they have effected its synthesis by heating with arsenic acid at 180°–200° the orthodiparatriaminotriphenylmethane obtained by Renouf (Ber 1885, 1304) by the action of dehydrating agents on a mixture of orthonitrobenzaldehyde and aniline (v also Ostrogovich and Silbermann, Chem Zentr. 1907, 1 1195). The commercial product is 'a mixture of the two derivatives, and in the form of the nitrates or hydrochlorides appears on the market as phosphine

Properties : -Chrysaniline crystallises with 2 mols of H_2O from 50 p c alcohol in golden-yellow needles, and from benzene with 1 mol. of benzene of crystallisation in golden-yellow scales, the latter melt, when placed in a bath heated at 150 160°, but when slowly heated lose the associated benzene, and melt, like the former, at 267° 270°. It is insoluble in water, and sparingly soluble in alcohol On oxidation with chromic acid, it yields acridine and when diazotised and boiled with alcohol is converted into phenylacridine (m.p. 164°). Tetrazo- compounds have been prepared, but their couple products with amines, phenols, &c., are not as good dyes as those obtained from chrysaniline and its salts (Trillat and de Raczkowski, Compt rend. 114, 1024). Formaldehyde reacts with chrysaniline, yielding an orange dyestuff similar to chrysaniline in its tinctorial properties (T. and de R. Compt. rend. 116, 1382) *Chrysophenol* $C_{19}H_{14}N_2O$, a yellow dye, is obtained when it is heated at 160°–180° with concentrated hydrochloric acid, and crystallises from dilute alcohol with 2 mols. of H_2O in ruby-red needles. Chrysaniline forms two series of salts ; of these, the sparingly soluble nitrate is the most characteristic : it crystallises in ruby-red needles, and is employed under various names as a valuable golden-yellow dye for silk, wool, and leather (v. ACRIDINE DYESTUFFS).

CHRYSANTHEMIN v. ANTHOCYANINS.

CHRYSAROBIN (B.P., U.S.P.) is a yellow crystalline mixture of substances obtained from *Araroba* or *Goa powder*. The latter varies in colour from primrose-yellow to bronze and purple, and collects, possibly as the result of oxidation of the resin, in the cavities of the

stems and branches of *Andira Araroba* (Aguiar) (N.O. *Leguminsæ*), a tree inhabiting the forests of Bahia (Aguiar, Pharm. J. [iii.] 10, 42; *cf.* Greenish, *ibid.* [iii.] 10, 814). The drug was formerly exported by the Portuguese to Goa, but its origin for a long time remained secret. Goa powder is usually mixed with woody fragments from which it is freed by sifting; it is sometimes termed crude chrysarobin. After extraction of Goa powder with organic solvents (benzene, chloroform) there is left behind on evaporation a yellow crystalline powder, introduced in 1875 by a Bombay firm under the name *Chrysarobin*, which has since been included under this name in the British and United States Pharmacopœias, and is used in skin affections.

Attfield (Pharm. J. 1875, [3] 5, 721) obtained chrysarobin in a yield of 80·84 p.c. of the crude drug, using benzene. Tutin and Clewer (Chem. Soc. Trans. 1912, 101, 290), by successive exhaustion with light petroleum, ether, chloroform, ethyl acetate, and alcohol extracted only 57·5 p.c. The residue consists of woody fibre, inorganic and resinous constituents, a little sugar, &c.

Chrysarobin was originally thought to be a pure, or nearly pure, substance; in reality it is a complex mixture, consisting chiefly of reduced di- and trihydroxymethylanthraquinones, which crystallise together and are difficult to separate by purely physical means. Later the name chrysarobin was applied to one of the pure constituents, but it is better to reserve this name for the commercial mixture. Tutin and Clewer found the following percentage composition for three samples of commercial chrysarobin :—

1. Chrysophanic acid (=chrysophanol) [1]	6·3	7·2	8·9
2. Emodin monomethylether [1]			
3. Emodin	trace	nil	nil
4. Crude anthranol of chrysophanic acid	26	46	62
5. Anthranol of emodin monomethyl ether	small amounts		
6. Monomethyl ether of dehydroemodinanthranol	41·1	13·4	17·7
7. Ararobinol	4·2	4·1	nil
8. Inseparable mixture of partly amorphous substances	23	30	12

The first three of these substances are anthraquinone derivatives (for their properties and constitution, *see* RHUBARB). Nos. 4 and 5 result from Nos. 1 and 2 respectively, by reduction; they are derivatives of anthranol (9-hydroxyanthracene). No. 6 is a less strongly reduced anthraquinone. No. 7, of unknown constitution, is also an anthraquinone derivative, related to No. 1.

Chrysophanic acid anthranol $C_{15}H_{12}O_3$ has the constitution

$$C_6H_3(OH){<}^{COH}_{CH-}{>}C_6H_2(OH)CH_3$$
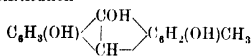
and was called chrysarobin by Jowett and Potter (Chem. Soc. Trans. 1902, 81, 1578). It is obtained from commercial chrysarobin by extraction with light petroleum; by shaking

[1] About 3 or 4 parts of the former to 1 of the latter.

its chloroform solution with sodium carbonate traces of emodin are removed, and after evaporation of the chloroform the residue is crystallised from much ethyl acetate, when it forms lemon-yellow scales, m.p. 202° (corr.) (regenerated from its acetyl derivative the substance melts at 204°). It is insoluble in sodium carbonate, soluble in caustic alkalis to a yellow solution, which becomes red by passing air through it, whereby it is oxidised to chrysophanic acid. The change is ·complete in 2 hours, as shown by measurement of the oxygen absorbed (Tutin and Clewer). The reverse change is brought about by hydriodic acid at 130°–140°. Chrysophanic acid anthranol dissolves in sulphuric acid with a yellow colour; it forms a diacetyl compound $C_{15}H_{10}O_3Ac_2$, m.p. 193°, and a triacetyl compound $C_{15}H_9O_3Ac_3$, m.p. 238°.

The *anthranol* of *emodin monomethyl ether* was not isolated by Tutin and Clewer as such, but its presence was inferred from aerial oxidation experiments, which converted it into emodin monomethyl ether.

The *monomethyl ether* of *dehydroemodinanthranol* $C_{16}H_{12}O_4$ is characteristic of chrysarobin. According to Eder (*v. infra*), its constitution is most probably :
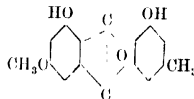
Tutin and Clewer converted it by boiling hydriodic acid into emodin anthranol, a substance containing a methyl group less and 2 hydrogen atoms more; by oxidation with chromic acid they converted it into emodin methyl ether.

Of the substances 1–6 chrysophanic acid had also been found by Attfield, its anthranol by Jowett and Potter, and emodin monomethylether by Oesterle and Johann (Arch. Pharm. 1910, 248, 476), but this was the full extent of the agreement among the various investigators of chrysarobin until Eder (Arch. Pharm. 1915, 253, 1; 1916, 254, 1) confirmed all the principal results of Tutin and Clewer. He oxidised the commercial substance with air in alkaline solution, and considers that hydrogen peroxide is formed in this reaction, and is responsible for further changes. He thus obtained the following percentages : emodin 0·2, emodin methylether 9·3, chrysophanic acid 22·7, dehydro-emodin anthranol monomethyl ether 18 (=chrysarobol of Hesse ?), amorphous products 26. It should be remembered that most of the chrysophanic acid and some of the emodin methyl ether were originally present as anthranols. In his second paper, Eder acetylated and benzoylated chrysarobin and obtained by subsequent hydrolysis up to 14 p.c. of chrysophanic acid anthranol, up to 9 p.c. of emodin anthranol monomethyl ether, and up to 4 p.c. of emodin monomethyl ether, but no chrysophanic acid. The chief discrepancy is that Eder did not find the last of Tutin and Clewer's substances, *ararobinol*. This, according to the latter authors, has the composition $C_{23}H_{16}O_5$, and forms yellow crystals, decomposing without melting at about

225°. It dissolves in alkali with a yellow colour, but, like the methyl ether of dehydroemodin anthranol, and unlike chrysophanic acid anthranol, it is not readily oxidised by air. It gives a delicate and characteristic reaction with sulphuric acid ; a mere trace forms an orange solution, which on gentle agitation gives intense blue streaks ; the solution then becomes green, and finally dull grey. Ararobinol gives a triacetyl derivative (decomp at 225°), is reduced by hydriodic acid to dehydroararobinol, and oxidised by chromic acid to chrysophanic acid, but not quantitatively.

With the exception of chrysophanic acid anthranol, Tutin and Clewer could find none of the substances described by Jowett and Potter They had access to the latter's specimens of ' dichrysarobin ' and its ' methylether ; ' the former they separated into substance 4, and emodin anthranol, the latter into the substances 4 and 5. A mixture of the latter substances is similar in composition and melting-point to ' dichrysarobin methyl ether,' which illustrates the difficulty of separating the constituents of chrysarobin by mere crystallisation

Chrysarobin is occasionally employed internally as a purgative. Léger (J Pharm. Chim. 1912, [vii | 5, 588) has suggested that for this purpose chrysarobin should be substituted for chrysophanic acid, since they both have the same purgative effect, and the latter is difficult to obtain in a state of purity. Probably the chief constituent of chrysarobin, chrysophanic acid anthranol, does not exert a purgative action until it has been oxidised in the alimentary canal (to chrysophanic acid), as is the case with aloïn (Meyer and Gottlieb, Experimentelle Pharmacologie, Berlin and Vienna, 1914, 198). The chief use of chrysarobin is, however, as an ointment in skin diseases (psoriasis), and the active constituent appears to be the anthranol of chrysophanic acid. According to Unna's experiments (Baudisch, Ber 1916, 49, 179), the only active synthetic substitutes are the anthranols of 1-hydroxy and of 1 : 8-dihydroxy anthraquinone. The latter, *(iquolin)*

HO HO HO
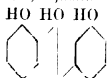
is more active in psoriasis than the anthranol of chrysophanic acid (chrysarobin), because it has not the dystherapeutic methyl group.,

Baudisch explains the effect of the 1 : 8-hydroxyls in accordance with Pfeiffer's views by the formula :
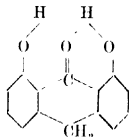
Various other substitutes have been suggested, e.g. acetyl chrysarobin (Knoll & Co. D. R. P. 105871 ; Chem. Zentr. 1900, i. 524), ' lenirobin ' ; eurobin is said to be triacetylchrysophanic acid (?).

' Dermol ' is prepared by precipitating a bismuth nitrate solution by a solution of chrysophanic acid in sodium hydroxide. 'Anthrarobin' is the anthranol of alizarin.

The different methods of extraction cause considerable variation in the composition of commercial chrysarobin and of its physiological action (Pharm. J. 1911, [iv.] 87, 630). Hence, Tutin and Clewer consider it fallacious to ask for compliance with exact requirements as to solubility, etc. (The U.S.P. states that 1 gram of chrysarobin dissolves in 385 c.c. of alcohol, 12·5 c c. of chloroform, 16 c.c. of ether, 30 c c of benzene, and 180 c.c. of carbon disulphide at 25°.) Pure chrysarobin dissolves in concentrated sulphuric acid with a yellow colour, and is insoluble in dilute sodium hydroxide ; concentrated sodium hydroxide dissolves it with a green colour. Chrysophanic acid, on the other hand, yields a red solution with concentrated sulphuric acid and dilute sodium hydroxide (Liebermann and Seidler, Ber. 11, 1603). Another method to distinguish chrysarobin from chrysophanic acid is to mix 0·05 gram with 0·2 0 3 gram sodium peroxide in a porcelain capsule, add 5 c c of alcohol, and after 5 minutes 15 c.c. of water. Chrysarobin yields a wine-lees colour, not destroyed by dilution with water, changing to yellow on the addition of acetic acid Chrysophanic acid yields a cherry-red colour, becoming brighter on dilution (Alvarez, Ann Chim anal. 1907, 9).　　　　G. B.

CHRYSATROPIC ACID *v.* LACTONES.

CHRYSAZIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS

CHRYSENE $C_{18}H_{12}$ or $\begin{array}{c}C_6H_4 \cdot CH \\ C_{10}H_6 \cdot CH\end{array}$

This hydrocarbon occurs in the highest boiling portions of coal tar, and in the tarry products obtained in the dry distillation of wood, fats, and oils (Laurent, Ann. Chim Phys. [2] 66, 136). Synthetically, it can be prepared by passing through a red-hot tube the vapour of benzylnaphthylmethane (Graebe and Bungener, Ber. 12, 1078), or those of cumarone and naphthalene, which condense with the loss of a molecule of water (Kraemer and Spilker, *ibid.* 23, 84), or by strongly heating indene For a complete synthesis, *see* Beschke, Winograd-Finkel and Kohres, Annalen, 384, 143.

Purification.—Chrysene is extracted from the mixture of solid hydrocarbons consisting chiefly of pyrene and chrysene, which boil at a higher temperature than anthracene, and constitute the last portions of the distillate from coal tar, by repeated digestion with carbon disulphide in the cold. This treatment removes all the hydrocarbons in the mixture except chrysene (present to the extent of 18–19 p.c.), and this is further purified by crystallisation from coal oil (b.p. 150°), from which it separates in golden-yellow scales The yellow colour, due to an impurity, cannot be removed by repeated crystallisation, but is destroyed by boiling with alcohol and a small quantity of nitric acid (Liebermann, Annalen, 158, 299), or most simply by the action of perchloric acid (K. A. Hofmann. Ber. 43, 1086).

A second method for obtaining chrysene from crude greenish-yellow anthracene (m.p. 207°–208°) has been described by Schmidt (J. pr. Chem. [2] 9, 250, 270). For this purpose, 40–50 grams of the anthracene are dissolved in 5 litres of strong (95 p.c.) alcohol, and the

solution, after filtration, is boiled with 30 grams of nitric acid (sp.gr. 1·4) in a reflux apparatus for some time. On cooling, red needles of a sparingly soluble compound of chrysene and dinitroanthraquinone $C_{18}H_{12},C_{14}H_6(NO_2)_2O_2$ separate, which, when treated with tin and hydrochloric acid, decompose into chrysene and reduction compounds of dinitroanthraquinone. The hydrocarbon is then obtained pure and colourless by crystallisation from benzene.

Properties.—Chrysene crystallises in scales, or in well-defined, colourless rhombic plates, which show a violet fluorescence, melts at 250° and boils at 448° (Schweitzer, Annalen, 1891, 193). It is a sparingly soluble substance; for example, 100 parts of absolute alcohol dissolve 0·097 part at 16°, and 0·17 part at 18°, and 100 parts of toluene dissolve 0 24 part at 18°, and 5 39 parts at 100° (*v* Bechi, Ber 12, 1978), whilst ether, carbon disulphide, benzene, and acetic acid dissolve it only to a slight extent at the ordinary temperature, but more readily on boiling The solutions, like the pure hydrocarbon, show a deep reddish-violet fluorescence. On adding chrysene to a solution of formaldehyde and sulphuric acid, a reddish-violet colour is produced, this is destroyed by the addition of water (Ditz, Chem. Zeit. 31, 445). The absorption spectrum of chrysene has been studied by Baly and Tuck (Chem. Soc. Trans 1902, 14) Chrysene combines with dinitro-anthraquinone and with picric acid (trinitro-phenol) to form characteristic compounds; the *picrate* $C_{18}H_{12},C_6H_2(NO_2)_3OH$, obtained by adding chrysene to picric acid in benzene solution, crystallises in long red needles, and is decomposed by alcohol (Liebermann, Schmidt). When heated with concentrated sulphuric acid, chrysene yields a sulphonic acid, and when treated with nitric acid, under varying conditions, yields mono-, di-, and tetra-nitro derivatives (*ibid.*), whilst chlorine and bromine convert it into substitution-derivatives (Schmidt). Aminochrysene is obtained by the reduction of nitrochrysene with phosphorus and hydriodic acid (Abegg, Ber 1893, 792), or with tin and hydrochloric acid (Bamberger and Burgdorf, *ibid.* 1893, 1006). On oxidation with chromic acid in acetic acid solution, chrysene is converted into *chrysoquinone* $C_{18}H_{10}O_2$, which crystallises in yellowish-red needles, melts at 235°, yields azines on treatment with ortho-diamines (Liebermann and Witt, *ibid.* 20, 2242), and is characterised by dissolving in concentrated sulphuric acid with a blue colour On oxidation with lead peroxide in alkaline solution the quinone is converted into β-phenyl-α-naphthoic acid, from which by elimination of carbon dioxide, β-phenylnaphthalene is obtained.

CHRYSEOLIN *v.* Azo- COLOURING MATTERS.

CHRYSIN, 1 : 3-dioxyflavone $C_{15}H_{10}O_4$, is obtained from poplar buds (Piccard, Ber. 1874, 88; and Darier, *ibid.* 1894, 21). It has been synthesised by treating phloracetophenone with ethyl benzoate in the presence of sodium, when 2 : 4 : 6-trimethoxybenzoylacetophenone is formed; on boiling with hydriodic acid, the methyl- groups are eliminated, condensation takes place with the production of 1 : 3-dioxy-flavones (Emilewicz, v. Kostanecki and Tambor, *ibid.* 1899, 2448; 1904, 3167). It is a yellow crystalline solid, melting at 275°. By heating it on the water-bath with methyl iodide and potassium methoxide, tectochrysin, which also occurs in poplar buds, is formed (Emilewicz, Kostanecki and Tambor, *l.c.*). Chrysin is a member of the quercetin series (Perkin, Chem Soc. Trans. 1896, 1443), and dyes cloth mordanted with aluminium a pure yellow; with chromium, an orange-yellow; and with iron, a pale chocolate (Perkin, *ibid.* 1897, 818).

CHRYSOBERYL. Aluminate of beryllium, $BeAl_2O_4$, crystallising in the orthorhombic system, and used as a gem-stone. It is usually met with in well-formed crystals, which as a result of twinning often simulate hexagonal forms, or as rolled pebbles in river gravels. Sp.gr 3·65-3·75; hardness 8½, taking the third place amongst minerals, being exceeded only by diamond and corundum. Few minerals are so resistant to chemical reagents as chryso-beryl; it is not attacked by acids nor fusible before the blowpipe, and is decomposed only by fused alkalis. The colour ranges in various shades of yellow and green. The variety *alexandrite* is emerald-green in daylight, but violet-red in lamp-light. Another gem variety, known as *cymophane* or 'oriental cat's-eye,' shows a bluish milky band of reflected light which travels across the convex polished surface as the stone is moved about. Chrysoberyl occurs embedded in granite and crystalline schists. Material of gem quality comes from Ceylon, Brazil, and the Urals. By reason of its high degree of hardness it has occasionally been used for jewelling watch-bearings. L. J. S.

CHRYSOCOLLA. A hydrated silicate of copper, sometimes of importance as an ore of copper. The formula is usually given as $CuSiO_3·2H_2O$, but the composition is variable, the mineral often being mixed with various impurities—silica, alumina, copper carbonate or phosphate, limonite, &c. On these differences in composition several trivial varieties have been distinguished by special names. The mineral is of secondary origin, occurring in the upper portions of deposits of copper ores. It forms encrusting or botryoidal masses, which may be vitreous and translucent, resembling opal or enamel in appearance, or dull and earthy. The colour ranges from bright green to bright blue, and there is a wide range in the sp.gr. 2·0-2·8. Under the microscope it sometimes shows a minutely fibrous structure, and small acicular crystals from Idaho have been described (J. B. Umpleby, 1914). Such material is optically uniaxial and positive with refractive indices 1·57 and 1·46; sp.gr. 2·4. Interbanded with the microcrystalline material is often some optically isotropic material, and for this amorphous equivalent of chrysocolla the name *cornuite* has been proposed (A. F. Rogers, 1917).

A variety known as *pitchy copper-ore* (Ger. Kupferpecherz), dark brown or black in colour and with the appearance of pitch, is of some importance as an ore of copper, particularly in Chile. It consists of a mixture of chrysocolla and limonite. Chrysocolla of the more ordinary type has been mined for copper in South Australia, Belgian Congo, Chile, Arizona, Idaho, &c. The name chrysocolla, from χρυσός, gold, and κόλλα, glue, was applied by the ancients to materials used for soldering gold, and included, besides certain copper minerals, also borax. L. J. S.

CHRYSOFORM. Trade name for dibromo-diiodohexamethylenetetramine.

CHRYSOGEN. An orange-coloured substance, containing more than 94 p.c. of carbon, and said to be a hydrocarbon, discovered by Fritzsche (Zeitsch. Chem. 1866, 139) in crude anthracene. It is sparingly soluble in the ordinary organic solvents. In sunlight, its solutions become rapidly bleached, and yield a colourless crystalline compound which, on fusion, becomes orange-yellow.

CHRYSOÏDINES *v.* Azo- COLOURING MATTERS.

CHRYSOÏN *v.* Azo- COLOURING MATTERS.

CHRYSOLITE *v.* OLIVINE.

CHRYSONAPHTHAZINE *v* AZINES.

CHRYSOPHANIC ACID (*Chrysophanol*) *v.* CHRYSAROBIN ; RHUBARB

CHRYSOPHENIN *v.* Azo- COLOURING MATTERS.

CHRYSOPRASE *v.* CHALCEDONY.

CHRYSOTILE *v.* ASBESTOS AND SERPENTINE

CHRYSOTOLUAZINE *v.* AZINES

CHRYSOTOLUIDINE $C_{21}H_{21}N_3$ A yellow crystalline base of unknown constitution (*cf.* Hofmann, Ber. 2, 380), occurring in the residue obtained in fuchsin manufacture by the arsenic acid method (Girard, De Laire, and Chapoteaud, Compt. rend. 63, 964 ; 64, 416). The hydrochloride is a yellow dyestuff

CHRYSYL. Trade name for zinc boroperate obtained by boiling together solutions of boric and picric acids with zinc oxide ; used as an antiseptic.

CHURCHITE. A hydrated phosphate of cerium (Ce_2O_3 51·87 p c) and calcium, occurring as grey fan-like aggregates of acicular crystals encrusting quartz and slate in a Cornish copper lode. Unfortunately nothing is known of the exact locality of the mineral. L. J S.

CHYMASE *v.* FERMENTATION

CICATRICINE. Trade name for a solution of thiosinamine, antipyrine, and lucaine lactate

CICUTOXIN $C_{19}H_{26}O_3$, the poisonous principle in water-hemlock (*Cicuta virosa*) is contained in the tubers to the extent of 0 3–0·4 p.c. It is found also in *C virosa*. It is a yellow resin-like substance which readily decomposes and polymerises above 50° D^{22} 0·9659 b_D^{25} 1·5885. Unites energetically with bromine and ignites spontaneously in contact with strong nitric acid. On dry distillation it yields an oil $C_{13}H_{21}O_2$ of sp gr 0·936 at 20°. Distilled in a current of steam it gives an oil $C_{14}H_{22}O$, of a pleasant odour ; it gradually polymerises to a transparent semi-solid resin On oxidation with nitric acid cicutoxin yields carbon dioxide, oxalic acid, hydrogen cyanide, isobutyric acid, and acetyl-2-cyclopentanone, b p. 735"/15 mm., Compounds of cicutoxin with lead, barium, hydrogen chloride, ammonia, bromine, and iodine are known. Cicutoxin appears to be a derivative of 4-pyrone (Jacobson, J. Amer Chem Soc 1915, 37, 916).

CIDER or **CYDER** is a vinous beverage produced by expressing and fermenting the juice of apples. Perry is a similar article made from pears. The two are very much alike in character, and, the principles of manufacture being generally the same for each, reference will be made to cider only in this article, except when occasion requires the special mention of perry.

The largest cider-producing country of the world is France, followed by England, Germany, the United States and Canada, and it is now also produced in increasing quantities in other countries, notably Ireland and Australia. In England the principal cider-growing districts are the counties of Somerset, Devon, and Hereford, smaller quantities being made in Gloucester, Worcester, Monmouth, Kent, and Norfolk. The mean annual production of the United Kingdom is estimated at 60,000,000 gallons, of a value of about 3,000,000*l*, including the Excise Duty of 4*d* per gallon.

The ordinary cider of commerce in England is a beverage of widely varying character. It may contain as little as 2 p c. or as much as 8 p c of alcohol by weight, depending on the quality of the apples from which it is made, and the process of its manufacture, particularly the stage at which the fermentation has been stopped. Apart from its characteristics of flavour, body, and colour, cider may be roughly divided into three classes or grades, viz : sweet, which has been only slightly fermented ; dry, well fermented , and medium, between the two. Apple juice of good average quality has a sp gr of about 1050 to 1055, corresponding to 10–12 p.c. of sugar As the fermentation produces, roughly, 1 p c of alcohol from every 2 p.c. of sugar, the following table shows the approximate comparative composition of apple juice, and the three grades mentioned :—

	Sp gr.	Sugar	Alcohol
Apple juice .	1050–1055	10–12 p.c.	—
Sweet cider .	1025 1035	6–7	2–3 p.c.
Medium cider .	1015–1025	4–5	3–4
Dry cider .	1000–1010	0–2	5–6

It must be understood that these figures are only approximate, and show the proportions of alcohol and sugar in cider made from apples of average quality, when the fermentation is stopped at the sp.grs. mentioned and no sugar is added.

The rough cider of the farmhouse, found in the south-western counties, is of a very dry grade, being fully fermented, no attempt being made to check the 'working,' while the ordinary cider (bottled and draught), found in the average hotel in cities, is a beverage which has been but slightly fermented, and is of the sweet to medium grade, the greatest public demand being for cider as a summer beverage, light, sweet, and refreshing. It must not be assumed, however, that all bottled cider is sweet, for it is obtainable from several firms of repute in four well-defined grades—sweet, medium, dry, and extra dry.

The raw material from which cider is made varies in composition and character as much as the cider itself. The majority of English orchards were originally stocked with almost innumerable varieties of apples and pears, most of them of inferior quality, for either table use or for the manufacture of cider or perry ; but great improvements have of late years been made in the planting and cultivation of the orchards, with a corresponding improvement in the quality of the beverages produced. Speaking generally, it may be said that good cider cannot be made from any but essentially vintage varieties of apples, most of which are quite

unsuited for table use because of their astringent flavour, due to the large proportion of tannin they contain. The majority of table varieties yield a juice deficient in sugar and tannin, with an excess of acidity, as compared with the vintage sorts, which are cultivated specially for the manufacture of cider. This is particularly applicable to perry pears, which are almost invariably very astringent in taste, although it is curious to note that the percentage of tannin they contain is not exceptionally high. To make good cider, the sp.gr. of the juice should not be under 1045, it should contain at least 0·15 p c. of tannin, which gives keeping and clearing properties, with an acidity not exceeding 0·5 or 0·6 p.c. of malic acid for sweet cider, and 0·3–0·4 p.c. for dry, while those substances which constitute ' body,' consisting of mucilage, albumen, salts, colouring matter, &c., are also of importance; but, having been very little investigated, it is impossible to state definitely what proportions of each are necessary. A high s₁ gr. with a correspondingly high sugar content, is generally considered the most important quality, but some apples are known to yield a juice high in sp gr. but deficient in colour and body (the two are usually associated), while others of a low sp gr but rich in colour and body, may produce cider of better quality than the first-mentioned. Too much reliance, however, must not be placed on the mere chemical composition of the juice as indicative of the value of an apple for cider making, the characteristic flavour of the variety and the rate of fermentation, which varies greatly with different juices, being at least equally important.

Vintage apples are roughly divided into three classes—sharp, containing normally not less than 0·45 p.c malic acid; sweet, containing normally less than 0 45 p c. of malic acid, and 0·2 p.c. of tannin; bitter sweet, containing normally less than 0 45 p c. of malic acid and more than 0·2 p c of tannin The following table shows typical analyses of the juice of several of the best of each class, together with that of a hitherto unknown and unnamed variety recently found in Somerset (' Butleigh No. 14 '), which is of outstanding merit.—

No.	Variety	Sp gr.	Malic acid	Tannin	Total sugar
1.	Kingston Black	1060	0·54	0·126	12·66
2.	Foxwhelp	1059	1·04	0·270	13·25
3.	Cowarne Red	1054	0·65	0·230	12·05
4.	Sweet Alford	1057	0·14	0·120	12·19
5.	White Jersey	1060	0·25	0·190	13·33
6.	Cherry Norman	1055	0·21	0·354	12·25
7.	Horner	1053	0·15	0·240	11·89
8.	Royal Jersey	1065	0·16	0·380	15·00
9.	Barland	1054	0·62	0·119	11·32
10.	Butt	1053	0·66	0·270	11·75
11.	Oldfield	1068	0·80	0·128	14·92
12.	'Butleigh No.14'	1104	0·24	0·258	22·22

Nos. 1, 2, and 3 are sharp varieties; 4 and 5, sweet; 6, 7, and 8, bitter-sweet; 9, 10, and 11, perry pears; 12, a bitter-sweet of unusually high quality.

The process of cider making is of very ancient origin, but modern scientific cider making may be said to date from the year 1893, when the Bath and West of England Agricultural Society instituted some chemical and bacteriological research into the subject, a work which was carried on by Mr. F. J. Lloyd for some seven years in Somerset, and has subsequently been continued on a more ambitious scale at the National Fruit and Cider Institute, associated with the University of Bristol, under the direction of Prof. B T. P. Barker. The results of these investigations form the foundation of modern cider making, and annual reports thereon constitute the most trustworthy literature on the subject.

Whereas the quality of the cider depends primarily on that of the apples used, the nature of the product is largely influenced by the methods of manufacture and fermentation, and general management. To ensure good quality, care of the apples in the orchard is essential, for no good beverage can be made from fruit which has been carelessly gathered or stored. It should be shaken from the trees when just ripe, bruising being avoided as far as possible, and stored in heaps (preferably under cover if the weather be wet), until it becomes soft and mellow, but not over-ripe, care being taken to avoid either washing by rain, which results in the loss of sugar and yeast, or heating, which produces fustiness in the cider, as well as a great tendency to acetic fermentation. When thoroughly mellow, the fruit is selected and blended in the proportions necessary to give the degree of sweetness, acidity, and astringency required for the variety of cider it is intended to make. Sweet cider is best made from a blend of sweet, sharp, and bitter-sweet apples; while dry cider should be made from a blend giving a minimum of acidity, with only a moderate proportion of tannin. Very few varieties of apples are individually capable of producing the finest cider, an appropriate blending being necessary. This does not apply to pears and perry making: single varieties, unblended, usually giving best results. In the actual processes of grinding the fruit and expressing the juice, steam or hydraulic power is generally used in modern factory practice, but, apart from economic reasons, this has no advantage over the old-fashioned hand-power machinery of former days. The fruit is ground to a fine pulp, called ' pomace,' which falls upon the press, is held together in thin squares by manilla or hempen cloths, and is usually pressed at once. In some places, however, the pomace is allowed to remain in tubs for 12 to 24 hours before pressing, which is said to improve the quality of the resulting liquor, but there seems to be no scientific reason for this custom, and investigations have failed to show that sufficient advantages are gained to compensate for the work it entails. With efficient presses, about 75–80 p.c. of the weight of apples is obtained as juice, and about 80 p.c. in the case of pears. The most profitable means of utilising the dry-pressed pomace is as cattle food. In France the juice is sometimes extracted by the ' diffusion ' process in use in the beet-sugar industry, but this does not meet with general approval, and has not been adopted in this country. The fresh juice is run into casks or open vats called

'keeves,' to undergo the important process of fermentation, which commences spontaneously in a few days, the time depending on the character of the juice and the temperature. An important question here arises : Shall the cider be allowed to undergo a natural fermentation, or shall a pure culture of yeast be added to dominate it ? At the present time this is a debatable point. While in France and Germany it is generally acknowledged that the use of pure cultures improves the quality of the liquor, and they are largely used, in this country and America it seems doubtful whether the advantages of their use are sufficient to compensate for the extra expense and trouble involved Pure yeasts, isolated from the best growths of cider and wine, have been cultivated and added in sufficient quantity to dominate the fermentation and prevent the various wild races from exercising much influence. (Owing to the difficulty of avoiding a cooked taste, sterilisation of the apple juice, even at comparatively low temperatures, is rather impracticable) The general results tend to show that fermentation by suitable yeasts give a somewhat superior product to that obtained by natural fermentation ; but the full advantages are not apparent until the cider is about a year old, whereas, in general practice, it is usual for it to be consumed before it attains that age. The use of pure cultures in the cider industry in this country is, for that reason, far from general, and it does not seem likely to make much headway in the present state of our knowledge of the subject Little is known of the various species of yeasts naturally occurring on the skin of the apple, which subsequently develop in the cider, forming the 'lees' at the bottom, and conducting the fermentation, but the largest number consist of forms allied to the *Saccharomyces Ellipsoideus, S. Pastorianus,* and *S. apiculatus* types. A fairly slow fermentation is generally desirable, but, on the other hand, it is one of the most important points in the whole process that the primary alcoholic fermentation be vigorous enough, and is not checked too soon, otherwise the cider is laid open to the attacks of numerous undesirable organisms, which will show their effects in various 'diseases' during the following summer The 'keeving' system of fermentation, in open vats with loose covers, is preferable to that in closed casks, as the 'head,' which is soon thrown up, consisting of yeasts and light portions of tissue, can be skimmed off from time to time. It is not advisable, however, to keep the cider in the keeves longer than about a week, lest incipient acetic fermentation set in, and, as soon as no further head is thrown up, it is racked into closed casks to complete the primary fermentation. The subsequent conduct of this important process is governed by the grade of cider it is desired to make, the hydrometer being in regular use for watching the fall of the sp.gr. The rate of fermentation depends partly on the character and composition of the juice, and partly on the temperature ; but these conditions are practically beyond control. Blending the apples to ensure the requisite degrees of sweetness and acidity in the juice will comply with one condition of a moderate rate, but as the proportion of nitrogenous matter is

of still greater importance, and is a subject on which, strangely enough, little is known, and no reliable figures obtainable, blending to ensure the proper percentage cannot be scientifically done at present. Regulating the temperature is also impracticable, for a large quantity of cider would have to be handled in a very short space of time, and this would be too expensive a process. A large plant would have to be fixed up, which could only be in use a few weeks each year, and possibly it might not be required at all. Whenever the sp.gr. approaches the point at which it is desired to stop the fermentation, the cider is racked off into clean casks, with or without sulphuring or the use of other preservative. This alone, however, is not usually sufficient to stop fermentation, unless an excessive quantity of preservative be used, or racking into sulphured casks be repeated several times. The best known means, which has the advantage of adding no materials of a questionable nature to the liquor, is to filter it through one of the many useful cotton-pulp filters now on the market Even the use of a filter is open to some objections, for it removes some of the body (probably of a colloid nature) and flavour from the cider. The clarification also presents great difficulty with many ciders, neither isinglass finings nor boiled apple pulp, which are commonly used for the purpose, having any effect, so that the filter, which clarifies the cider, and at the same time stops the fermentation, is preferred, in the absence of anything better, for this purpose Depending on various circumstances, the cider is filtered and stored away to mature in casks, at any time from two to four or even six months from the time of making. If filtered perfectly bright, and stored in clean casks, kept well filled, it will 'keep its sweets' for a whole season or longer, with the loss of only a few degrees of sp gr, even though it may contain as much as 6 or 7 p.c of fermentable sugar. During this period of storage, it mellows and develops its fragrant aroma and delicate flavour, and also loses a certain proportion of its acidity and astringency. The strongest and best cider will keep in cask for some years, but that of average quality is at its best within the first year. It keeps best and improves most in bottle, but only cider of good and sound quality should be bottled ; it should have an original gravity of at least 1050, should undergo a vigorous primary fermentation, and be perfectly brilliant when bottled. The best age for bottling is from four to six months, and if not more than a year old at the time, it will develop sparkling condition like champagne after a few weeks' storage. The carbonating process of bottling is becoming more general, and there seems to be no objection whatever to its use, some of the best brands on the market having been treated in this way.

Matured cider is liable to several disorders or 'diseases,' the principal being acetification, 'sickness,' ropiness, and blackening. Like all liquors of low alcoholic strength, it is particularly apt to acetify on very slight provocation, and for this reason, exposure to air at all stages of manufacture is to be avoided. 'Sickness' is a recommencement of alcoholic fermentation, which is set up during the summer following its manufacture, and may occur in cask or

bottle. The cider becomes very turbid, and the production of alcohol is accompanied by the development of a most disagreeable smell and flavour, due, it is thought, to formation of acetaldehyde, together with an increase in acidity, partly lactic and partly acetic, which renders the liquor quite undrinkable. It is a source of great loss, for it usually attacks the richest and most fruity ciders, and is due to the action of several special organisms, contributing causes being a deficiency of malic acid in the juice, and a weak primary fermentation. Ropiness is not so frequently met with, and little is known of its causes in cider; but it is generally found where there is a deficiency of tannin. Some ciders turn dark very quickly on exposure to air, some almost black in less than half an hour. This may be due either to an excess of iron acquired from the soil on which the apples are grown, but more often from the utensils used in the making, or to enzymic action; the use of a little preservative often prevents its development.

A standard of chemical composition for what is sold as cider has been formulated in some countries, but not in Great Britain. Owing to the extreme variations in the character and composition of genuine cider, it is almost, if not quite, impossible to fix a definite chemical composition and say that it represents what should be considered a standard cider. For this reason, the standard fixed in foreign countries is necessarily very low, but while it probably admits of a certain amount of adulteration, it no doubt acts as a check. It can hardly be contended that nothing should be sold as cider which is not the pure juice of apples. Brewers, wine makers, and distillers are not restricted by law to the use of malt and hops, grape juice and malt respectively, in the making of their products, so that a law to limit cider makers to the use of apples only would operate unfairly against them as compared with the other trades mentioned. It has been stated that many varieties of cider apples grown in this country are not capable of making first-class cider, and the better sorts are in too small a minority to meet the demand. In poor vintage seasons, also, the general quality is low, sugar being deficient and acidity excessive It is also undoubtedly true that cider made from the poorer varieties of apples, and in poor vintage years, is capable of great improvement by the addition of a certain proportion of cane-sugar syrup, as is done in the process of 'gallisising' wines, to obtain the correct proportion of acidity to sugar. It is difficult to say what maximum proportion of this syrup should be allowed, but there is seldom any occasion for the use of more than 10 p.c. to make the cider suitable for the English market. The fact that there are so-called 'ciders' on the market, which are innocent of a drop of apple juice, shows the necessity for some sort of standard. Generally speaking, it may be concluded that no cider can be considered genuine which does not contain at least 2 p.c. of alcohol by weight, or which does not show an original gravity of 1045 or upwards. Another vexed question is that of the use of preservatives, some people contending that it is impossible to do without them, and others that they are not necessary if the cider be well and carefully made. There is much to be said on both sides. Some makers sulphur their casks, thus adding a certain quantity of sulphurous acid to the cider; but it is generally considered, though very strangely, that this does not constitute the addition of any 'chemicals.' Others use sulphites or salicylic acid, and justify their use by the argument that all cider, no matter how carefully made, is peculiarly susceptible to the various 'diseases' previously mentioned, and has often to be kept under conditions which render them unpreventable by any other known means, for example, on draught in a warm bar, perhaps for some weeks. There is certainly a great deal of reason in this, and it would probably be a hardship to absolutely prohibit the use of any preservative, but, on the other hand, they are sometimes used in needlessly excessive quantities, which, in the interest of the public health, should be avoided. The consumption of cider is rapidly increasing, due partly to its being recommended by medical men, and if it is to hold its own as a popular, and above all as a healthful, drink, it must be kept free from any ingredients of doubtful physiological effects.

Appended are analyses of a few typical ciders of well-known makes :—

Description	Sp gr	Alcohol by weight	Total acid	Total solids	Ash
Sweet sparkling	1025	3·65	0·24	5·98	0·245
Standard dry	1006	4·90	0·31	3·25	0·314
Standard sparkling	1015	3 90	0·53	6·00	0·360
Champagne perry.	1013	3·75	0 35	4·80	0·390

W. D. McC.

CIGNOLIN. Trade name for 1·8-dihydroxyanthranol. Used as a remedy for psoriasis. Has a more energetic action upon the skin than its 3-methyl derivative, chrysarobin (*q.v.*), (Unna, Dermatol Wochenschr. 1916, 62, Nos. 6–8).

CINCHOMERONIC ACID *v.* BONE OIL.

CINCHONA ALKALOIDS. The Cinchona Barks. 1. *Their Discovery.*—The febrifuge properties of the bark of the cinchona trees growing on the slopes of the Andes was probably known to the native Incas long before its curative properties became known to their Spanish conquerors. The earliest mention of a 'cure' is by Jussieu in 1600. The introduction of the bark to European countries was due to the Countess of Chinchon, wife of the Viceroy of Peru, who having been cured of an attack of fever at Lima in 1638, on her return to Madrid in 1640, brought with her some of the precious bark, and administered it to fever-stricken patients on her Spanish estates. It is in her honour that Linnaeus named the species 'cinchona.' For nearly 200 years the drug was administered in the form of a decoction of powdered bark, and the alkaloids in it were not isolated till 1816, when Gomez discovered the alkaloid cinchonine, followed by Pelletier and Caventou, who isolated quinine.

2 *The natural Cinchona Trees* occur in a long but very narrow belt on the slopes of the Andes, stretching from Columbia in the north,

through Ecuador and Peru to Bolivia on the south. For the greater part of the last century the trees were ruthlessly cut down and the bark stripped from them by the Indian collectors, no attempt being made to replace them or cultivate seedlings, and consequently the species was being rapidly exterminated when more scientific methods were gradually introduced.

The trees were first classified botanically by Weddell, in 1849, and in 1860 John Eliot Howard, F R.S , brought up-to-date and translated the notes of the Spanish botanist Pavon (compiled in 1800), under the title of the ' Nueva Quinologia of Pavon,' and these two books still maintain their position as the standard works on the subject. In 1880 Sir Clements Markham published a most comprehensive work entitled ' Peruvian Bark,' and it is from this book that the compilers of these notes have obtained much of their information The following table shows the locality and the botanical species of the various commercial barks on the London market in about 1870, and the analyses given, except when otherwise stated, were made by the present authors, of typical commercial samples which had been preserved in a collection of that date.

TABLE I.—THE NATURAL BARKS OF COMMERCE OF 1870

Commercial name	Botanical name	Locality	Discoverer	Typical analyses Percentage of alkaloids present					
				Quinine	Cinchonidine	Quinidine	Cinchonine	Amorphous alkaloid	Total alkaloids
Crown Barks	Cinchona officinalis	Loxa (S Ecuador)	Caldas, 1803	3 09	1 34	0 14	0 32	0 59	5 48
Red Barks	Cinchona succirubra	Chimborazo (Central Ecuador)	Condamine, 1738	J E. H (1870) Quinine . 1·50 Cinchonidine and quinidine 1 22 Cinchonine . . . . . 1 25 Total alkaloids . . 4·37 p c.					
Columbian Barks	Cinchona pitayensis	Pitayo (Columbia)	Mutis, 1772	—	—	—	—	—	—
Hard Pitayo	,,	,,		2 42	0 19	0 82	0 98	2·25	6·66
Soft Pitayo	,,	,,		1·91	0 16	0 77	1·28	1 50	5·62
Soft Columbian W. Coast	Cinchona lancifolia	Santa Fe and New Grenada		1 42	0 36	0 09	0 35	0·65	2 87
Carthagena	Cinchona cordifolia	Carthagena and Guiaquil		1 31	0 41	0 03	0 07	0·40	2·23
Grey Barks	Cinchona nitida Cinchona micrantha Cinchona Peruviana	Huanuco (N. Peru)	Renquifo, 1776	J. E. H. (1862) ' Nearly 2 p.c. of cinchonine.' J. E. H. (1862) Cinchonine 2 p.c. Total alkaloid 2·7 p.c . J. E H (1862) Quinine 0·45 p.c. Cinchonine 0·9 p.c.					
Yellow Barks	Cinchona calisaya	Bolivia and S Peru	Haenke and Cels 1776	2·00	0·46	0·20	0·56	0·90	4·12

Note.—The analyses marked J E. H. are from records of John Eliot Howard. The results must be accepted with reserve, as at the date mentioned, the methods of separation of the different alkaloids were very rudimentary.

3. *Transplantation and Cultivation.*—In the middle of the last century the necessity of dealing adequately with the devastations of malaria in India and the diminishing supply of natural cinchonas, directed attention to the importance of their cultivation in suitable districts in that country.

In 1859 Sir Clements Markham organised expeditions to South America for the purpose of securing seeds of all the cinchonas then of

commercial importance. He himself headed a search for calisaya seeds in Peru and Bolivia. Spruce collected succirubra in Ecuador, while Pritchett was responsible for the grey barks of Huanuco in Peru. In order to complete the series further expeditions under Cross were carried out in 1861 for officinalis bark from Loxa (S. Ecuador), in 1868 for Pitayo bark from Columbia, and a final search in 1877 for soft Columbian and Carthagena barks.

Markham's narrative of these expeditions tells of the immense difficulties which were surmounted by these public-spirited pioneers, not only from the actual hardships of the expeditions, but also from the suspicious and often actively hostile attitude of the Indians, and to crown all, the problem of transporting the collections to the coast, and carrying them alive to England, and subsequently through the Red Sea to India.

All these difficulties were, however, overcome, and a large proportion of the seedlings survived the ordeal and were successfully planted in the Nilgiri Hil's in 1861, under the superintendence of MacIvor. The cultivation of cinchona in India from MacIvor's seedlings rapidly spread, and plantations were established by private owners in the Nilgiris, and in the Palni Hills of Travancore. In 1865 plantations were established at Hakgala in Ceylon and in Coorg, followed shortly after by further enterprises at Wainad, Mysore ; Darjiling in Sikkim ; and the Karen Hills in Burmah MacIvor introduced two methods of harvesting the bark :—

1. Coppicing and allowing the tree to shoot again from the same trunk ; and

2. 'Renewing ' by mossing. In the latter process the bark was removed in longitudinal strips about an inch wide, leaving a space untouched between each strip denuded of bark The tree was then bound round with moss and the bark allowed to 'renew' and cover the wounds. This method, although more laborious than coppicing, largely increased the yield of each tree. David Howard (J. Soc. Chem. Ind. 1906, 26, 97) states that renewed bark is richer in alkaloids than the original, and that the proportion of quinine to other alkaloids is increased.

In 1880, when Markham's book was published, the Indian plantations gave every promise of becoming the main source of supply for the markets of the world.' The fact that India does not find herself to-day in that fortunate position is shown in the following table, and the cause in the next paragraph.

A summary of sources of bark sold in European markets :—

	In 1880	In 1911
Columbia .	6,000,000 lbs.	
Bolivia, Peru,		35,200 lbs.
Ecuador .	960,000 lbs.	
India . .	1,170,000 lbs.	458,600 lbs.
Java . .	70,000 lbs.	19,778,000 lbs.
Jamaica .	21,000 lbs.	nil.
Africa .	nil.	25,400 lbs.

The explanation obviously rests on the rise of Java as the greatest cinchona producer, and it is therefore necessary to sketch briefly the history of this wonderful success of the Dutch in their principal colony.

The first attempt at cultivation in Java in 1852 ended in complete failure through the poor alkaloid-producing characteristics of the varieties of cinchonas of which seedlings were secured from South America ; the only trees producing a tolerable yield being a small number obtained from MacIvor's plantations in the Nilgiris. In 1855, however, Charles Ledger secured some seeds of Cinchona calisaya, half of which were planted in India and half in Java. Those in India failed, owing either to the climatic conditions or the mismanagement of the plantations after MacIvor's death. Those in Java, however, flourished exceedingly, and have produced a wonderful strain of trees, which, by skilful scientific cultivation, have produced, and are producing, bark containing up to 10 p.c. of quinine, and which have, therefore, far surpassed any other variety in its market value from a manufacturing standpoint.

4. *Hybridisation and Grafting.* — David Howard (J. Soc. Chem. Ind. 1906, 25, 97) deals with the effect of hybridisation (partly deliberate and partly accidental) on Java barks, and mentions a very common hybrid of commerce known as Robusta, a hardy growth, which nearly rivals Ledgeriana in its alkaloid value. Regarding grafting, he states that the 'Enten Baast' of commerce, from Java, is the result of grafting Ledgeriana on to a Succirubra stock, the bark from branches giving the characteristics of Ledgeriana, while the root bark retains the proportion of alkaloids common to Succirubra.

From a large experience of analysis of samples from different parts of the same cinchona trees, he found that the elaboration of alkaloid takes place solely in the downward course of the sap, and that the percentage of alkaloid increases in the bark from the twigs down the stem to the ground ; in the less flourishing trees the root bark being richest in alkaloid value, but of this alkaloid, the proportion of quinine and cinchonidine is lower, while that of cinchonine and quinidine is higher.

5. *The Commercial Aspect.*—In the same paper David Howard shows that the conquest of the world's markets by the Java planters was due to the careful and scientific work of Moens and others in the cultivation of the phenomenally rich Ledgeriana to the exclusion of the lower alkaloid-producing varieties, which enabled the Dutch growers to hold on during a period of about 20 years of bitter competition and low prices, which gradually ousted a large number of the older established, but less scientifically managed, Indian plantations from the market.

To emphasise the effect of successful Java cultivation the table given below shows two analyses : A, typical of the very best natural Calisaya bark produced from wild trees in about 1865 ; and B, of a typical good quality cultivated Ledgeriana bark sold in Amsterdam in May, 1914 :—

	Quinine	Cincho-nidine	Quini-dine	Cincho-nine	Amor-phous	Total alkaloids
	p c.	p c.	p.c	p.c.		
A	3·615	0·75	0·165	0·34	0·93	5·80
B	7·92	0·105	0·08	0·085	0·91	9·10

This shows the triumph of skilful cultivation in producing an enormous alkaloid yield of

almost pure quinine, over the best unaided efforts of nature.

6. *Other Bark-producing* countries only require a passing mention. The barks formerly produced by Jamaica and Mexico have disappeared from the market. The Portuguese possessions in West Africa produce bark regularly, the best-known source being the island of St. Thomé. South America still produces a considerable amount of bark, presumably now entirely from cultivated and not natural sources. A start was made shortly before the war in German East Africa, and although the plantations are at present small, the analysis of the samples shown below, if they can be regarded as typical, indicate very promising conditions, being in quality well up to the best Java production.

PERCENTAGES OF ALKALOIDS PRESENT.

Samples from German East Africa	Quinine	Cinchonidine	Cinchonine	Quinidine	Amorphous alkaloid	Total alkaloids
Ledgeriana	3·81	0·00	0·04	0·00	1·15	5·00
Hybrid	8·41	0·00	0·97	0·00	1·92	11·30
Succirubra	2·54	2·05	2·14	0·00	1·59	8·32
Robusta	2·66	3·51	0·28	0·00	1·16	7·61

7. *Other Trees producing Cinchona Alkaloids.* —Two other varieties of trees must be mentioned which, although belonging to the Remijia species, and not being botanically cinchonas at all, yet contain alkaloids of the cinchona group, which will be mentioned below.

Bark of the Remijia pedunculata, known as 'Cuprea Bark,' was sold in considerable quantities on the London market in the early eighties, and its analysis is interesting, as being the only natural bark known which contains quinine and other alkaloids (including the rare alkaloid cupreine), but absolutely no cinchonidine

The Remijia Purdieana contains interesting but rare members of the family of cinchona alkaloids, viz. cinchonamine, chairamine, conchairamine, chairamidine, and conchairamidine, the peculiar properties of which will be mentioned later.

REMIJIA PEDUNCULATA ('CUPREA') BARK.

	Sample A	B	C
Quinine alkaloid	1·38	1·27	1·20
Cupreine	0·11	0·05	
Quinidine	0·40	0·41	0·25
Cinchonine	0·22	0·26	0·27
Cinchonidine	nil	nil	nil
Amorphous	1·31	1·01	1·17
Total alkaloid	3·42	3·00	2·89

REMIJIA PURDIEANA BARK.

Cinchonamine nitrate . . 0·30 p.c.
Nitrate of other paricine bases 3·30 ,,

There is one variety of cinchona which, although valueless from a commercial point of view, since it contains none of the four alkaloids of commerce, has yet provided a considerable field for research, as several rare members of the cinchona alkaloid family have been extracted from it. It is described by Markham under the name of Pubescens, but was also called Pelleteriana (after the discoverer of the quinine base) and Cusco bark in commerce.

It would appear to have been widely distributed over the forests of Peru, and was found to be growing freely by Markham in the Caravaya district. The alkaloids isolated from it are cusconine, cuscondine, cuscamine, cuscamidine and aricine (called after Arica, the coast town from which it was exported).

Before leaving the subject of barks, the tree Aspidosperma Quebracho, a member of the Apocynaceæ, must be mentioned. This was considered by Hesse (Annalen, 1870, 154, 287) to be identical with the Quina Blanca of Mutis.

Two alkaloids have been extracted from it, Paytine and Paytamine (so called from the port Payta in North Peru), which although not actually classified under any group of cinchona alkaloids, have a very similar empirical formula, and possess certain febrifuge properties which justify their inclusion under this heading.

Principles of Cinchona Barks.—The following are the names and formulæ of the alkaloids occurring naturally in these barks, isomers being bracketed together :—

1. Cinchonine
2. Cinchonidine   } $C_{19}H_{22}ON_2$
3. Cinchonicine (cinchotoxin)
4. Hydrocinchonine (cinchotine)
5. Hydrocinchonidine (cinchamidine)   } $C_{19}H_{24}ON_2$
6. Cinchonamine
7. Cupreine $C_{19}H_{22}O_2N_2$
8. Quinamine
9. Conquinamine   } $C_{19}H_{24}O_2N_2$
10. Quinine
11. Quinidine   } $C_{20}H_{24}O_2N_2$
12. Quinicine (quinotoxin)
13. Hydroquinine
14. Hydroquinidine   } $C_{20}H_{26}O_2N_2$
15. Chairamine
16. Conchairamine   } $C_{22}H_{26}O_4N_2$
17. Chairamidine
18. Conchairamidine
19. Aricine
20. Cusconine   } $C_{23}H_{26}O_4N_2$
21. Concusconine
22. Dicinchonicine $C_{38}H_{42}ON_4$
23. Diquinicine (diconquinine) $C_{40}H_{46}O_3N_4$
24. Javanine
25. Cusconidine
26. Cuscamine   } formulæ not determined
27. Cuscamidine
28. Paricine $C_{16}H_{18}ON_2$
29. Paytine
30. Paytamine   } $C_{21}H_{24}ON_2$

These are combined in the bark mainly as quinates and cinchotannates with quinic acid $C_7H_{12}O_6$, and cinchotannic acid $C_{14}H_{16}O_9$; the former occurring to the extent of 5–8 p.c., and the latter 3–4 p.c. in the barks. Quinovic acid $C_{12}H_{48}O_8$ and oxalic acid (as the calcium salt) are also present in small amounts. The

quinates are soluble in water, but the cinchotannates only slightly soluble, dilute acids, however, decomposing them and effecting solution. The colouring matter in the bark is cinchonared $C_{19}H_{14}O_7$, occurring to as much as 10 p.c. It is soluble in alkalis, being reprecipitated by acids. Two glucosides, α-quinovin and β-quinovin, are usually present in all cinchonas, and give on hydrolysis quinovic acid and quinovose, a sugar isomeric with rhamnose (Liebermann and Giesel, Ber. 1883, 16, 926). The neutral bodies, cinchocerotine, and the isomers, cupreol and emchol $C_{26}H_{34}O + H_2O$ (Hesse, Annalen, 1884, 228, 288 ; 1886, 234 375), together with cholestol (Thoms, Arch. Pharm. 1897, 235, 39), appear to be constant constituents of cinchona barks.

The *ash* of these barks falls usually between 3 p.c. and 4 p.c , a curious fact being that the greater the altitude at which the bark is grown the higher is the ash In Indian barks the highest ash is found in Crown barks grown at 7000-8000 feet above the sea, falling in red barks grown at 5000-6000 feet, a minimum ash being found in Ledger bark, which grows at an altitude of 3000-5000 feet (Hooper, Pharm. J. 1886, 17, 545).

Constitution of the Cinchona Alkaloids.— Only a short account of the great amount of work done on this subject can be given here ; for fuller details, consult ' Vegetable Alkaloids,' by Pictet (Biddle, 1904), ' Die Konstitution der Chinaalkaloide,' by Comanduci (Sammlung chem u. chem. Vortrage, 1911, 16 ; Bande, 4 7), and Rabe's and Kaufmann's articles in the Berichte and Annalen since 1907.

The construction of *cinchonine* has been the most fully investigated of these alkaloids, and its relation to the other common alkaloids being simple, it is an easy matter to deduce their constitution from that of cinchonine

Cinchonine $C_{19}H_{22}ON_2$ is a ditertiary base forming *di*-alkyl iodide addition products On distillation with potassium hydroxide it gives, as the main product, quinoline, and a smaller amount of lepidine (4-methylquinoline), showing that cinchonine has a methylquinoline nucleus. Cinchonine may therefore be written

$$C_9H_6N \cdot C_{10}H_{16}ON$$
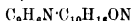
On treatment with the halogens, or haloid acids, it forms addition products, taking up 2 atoms of halogen or 1 molecule of acid, a fact pointing to the presence of a vinyl group. By the action of permanganate in the cold, a body, cinchotenine, which does not contain the vinyl group, is formed, and an atom of carbon is split off as formic acid, thus :

$$C_9H_6N \cdot C_8H_{13}ON(CH : CH_2) + 4O$$
<div style="text-align:center">Cinchonine</div>

$$\rightarrow C_9H_6N \cdot C_8H_{13}ON \cdot COOH + H \cdot COOH$$
<div style="text-align:center">Cinchotenine   Formic acid</div>
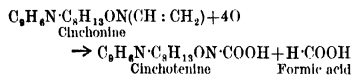
The vinyl group probably exists, therefore, in a side chain. Cinchonine and cinchotenine both contain a hydroxyl group, giving mono-acetyl derivatives. This completes the knowledge of the simpler groups in cinchonine, which can now be written $C_9H_6N \cdot C_8H_{12}(OH)(CH : CH_2)N$. There remains the constitution of the C_8H_{12} portion to be elucidated, together with the positions of the hydroxyl and vinyl groups.

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Now, on oxidising cinchonine with chromic acid, the molecule is split in two, yielding about one-half its weight of cinchonic acid $C_{10}H_7O_2N$ (4-carboxyquinoline) ; and about half its weight of a syrupy mass consisting of a primary body, meroquinene $C_8H_{14} \cdot COOH \cdot N$, and its secondary oxidation products, cincholoiponic acid

$$C_8H_{11}(COOH)_2N$$
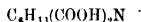
and loiponic acid $C_5H_9(COOH)_2N$. Cinchoninic acid is evidently the product of the methylquinoline nucleus, and the other three acids the product of the ' second ' half of cinchonine. The primary oxidation product of the ' second ' half, meroquinene, throws much light on the constitution of this portion of the cinchonine molecule, and is known to have the formula :
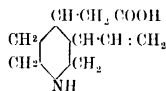
Now meroquinene is a secondary base, but as cinchonine is ditertiary, meroquinene must be derived from a portion of the ' second ' half, having the formula :
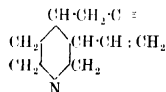
This and the quinoline portion account for $C_{18}H_{19}N_2$ of the cinchonine molecule, and there remains but $CH_3(OH)$, for which positions must be found.

On heating cinchonine with acetic acid it undergoes isomeric transformation into cinchonicine, a molecular rearrangement in which the hydroxyl group vanishes, and a carbonyl group appears, the tertiary character of the ' second ' half becoming secondary at the same time. This is a change which Rabe's researches have shown to be effected by this grouping :—

$$-CH(OH)-CH-N- \rightarrow -CO-CH_2 \cdot NH$$
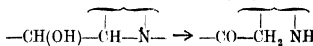
This supplies the last link required in the cinchonine molecule, which may now be formulated as the basis of the cinchona alkaloids :—
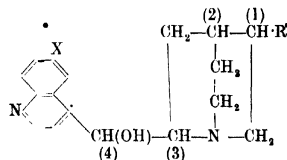
In cinchonine, cinchonidine, cinchonicine, quinine, quinidine, and quinicine $R = -CH : CH_2$.

In hydrocinchonine, hydrocinchonidine, hydroquinine, and hydroquinidine $R = -CH_2 \cdot CH_3$.

In cinchonine, cinchonidine, cinchonicine, hydrocinchonine, and hydrocinchonidine $X = H$.

In quinine, quinidine, quinicine, hydroquinine, and hydroquinidine $X = OCH_3$.

In cupreïne $X = OH$ (with phenolic properties).

Cinchonicine and quinicine have the ketonic grouping at carbon 4, as indicated above.

The numbered carbon atoms are asymmetric ; and the isomerism among these alkaloids is frequently due to the spatial arrangement around the carbon atom 3, since the asymmetry of the other three carbon atoms 1, 2, and 4 may be destroyed without interfering with the isomerism of the products (Rabe, Annalen, 1910, 373, 85).

It may be noted here that in the ditertiary bases fluorescence only occurs in those in which $X = OCH_3$, or a higher alkyl group. The toxicity of these alkaloids also appears to increase as the alkyl group in the X position increases from methyl to octyl.

The known conversions of one alkaloid into another may be given.

Cinchonine or cinchonidine on heating with moderately strong sulphuric acid is converted to cinchonicine ; quinine or quinidine yielding on similar treatment quinicine (Pasteur, Compt. rend. 1853, 37, 110, 166)

By heating cinchonine in amyl alcohol solution with potassium hydroxide part is converted to cinchonidine (Konigs and Husman, Ber. 1896, 29, 2185).

Cupreine is converted to quinine by heating at 100°C. under pressure with sodium and methyl chloride in methyl alcohol solution (Grimaux and Arnaud, Compt. rend 1891, 112, 776, 1364). Similarly, higher alkylated bodies may be prepared. Hydroquinine, when heated under pressure to 140° with hydrochloric acid, sp.gr. 1·125, or boiled with hydrobromic acid sp.gr. 1·49, or hydriodic acid sp.gr. 1·7 is converted to hydrocupreine, its methoxyl group being replaced by —OH (Hesse, Annalen, 1887, 241, 255 ; Pum, Monatsh. 1895, 16, 73).

The hydro- bases (in which $R = —CH_2.CH_3$) may be prepared from their respective unsaturated alkaloids, dissolved in dilute sulphuric acid, by the action of hydrogen under pressure in the presence of palladium black (Eng Pat. 3948, Feb. 16, 1912). Cinchonicine has been converted to cinchonine by Rabe (Ber 1908, 41, 67 ; 1911, 44, 2088).

Kaufmann and Huber have converted hydrocinchonicine into a mixture of hydrocinchonine and hydrocinchonidine (Ber. 1913, 46, 2913).

No complete synthesis of any of the cinchona alkaloids has been effected, although bodies very closely related to them both in structural formulæ and medicinal properties have been obtained (Ber 1913, 46, 1032 and 1823 ; 1917, 50, 144). Robinson has suggested by an ingenious method a possible phytosynthesis of these bases from formaldehyde, ammonia, and an acetone derivative. It is interesting to note that Perkin discovered the aniline dyes whilst trying to synthesise these bases.

Therapeutic Value.—The first work of importance on the comparative therapeutic effect of the various alkaloids was in 1868. when an Indian medical commission reported on the relative efficiency of the four principal alkaloids then commercially obtainable in .the treatment of malaria. This commission placed the alkaloids in the following order of efficiency :

1st { Quinine. / Quinidine.
3rd Cinchonidine.
4th Cinchonine.

At about the same time, J. E. Howard reported, as a result of his administration to patients suffering from the mild English malaria or ague still common at that time in the Essex marshes, that he considered quinine and cinchonidine equally effective, and cinchonidine and quinidine somewhat less satisfactory. Of late years the researches establishing the constitutional formulæ of these alkaloids has led pharmacologists to study the particular arrangement of the groups in the molecule which has the greatest effect in malaria prophylaxis and other uses of quinine, and these researches, though at present incomplete, are being actively pursued in various directions.

The modern uses of the cinchona alkaloids may be divided roughly under four headings.

1 *In small doses as a tonic and stomachic.*

2. *As an antimalarial remedy,* acting as an agent that will destroy the malaria parasite. The most comprehensive work hitherto published is that of Major A. C. MacGilchrist (Indian Journal of Medical Research, 1914, 2, 315 and 516 ; 1915, 3, 1).

About one-third of the quinine ingested undergoes cleavage of the molecule in the body, but whether it is this decomposed portion or the remaining two-thirds of the dosage which possesses its antimalarial properties appears not as yet to have been determined. The cleavage would appear to be the breaking off of the 'loiponic ring ' (or second half) from the quinoline ring portion of the molecule, the former yielding some such nucleus, as is described by Koenigs under the name of ethyl-quinuclidine

$$CH$$
$$H_2C \; CH_2 \; CHC_2H_5$$
$$CH_2$$
$$H_2C \quad CH_2$$
$$N$$
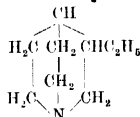
It would appear that the methoxy group or —OCH_3 side chain of quinine and hydroquinine render the specific action greater than those alkaloids, such as cinchonine and cupreïne, which do not possess it. Following up this side chain theory, efforts have been made to prove that by increasing the value of this group as in ethyl hydrocupreïne, or its more highly alkylated homologues, the antimalarial effect is still further increased. Results have not so far been very conclusive, and the point remains to be established in the future.

Another channel in which much investigation has recently been conducted is in the quinotoxin group of compounds. These have for many years been administered as a febrifuge under the name of quinoidine, which is really a mixture of quinicine, cinchonicine, diquinicine, and dicinchonicine. The present researches, which are being carried out with the individual bases obtained in as pure a state as possible, depend upon the theory that the quinicine or quinotoxin molecule, for instance, owing to the opening up of the ' loiponic ring,' possesses

a greater specific action than the corresponding 'saturated' molecule.

These researches are still incomplete, but if the fact were established that, owing to its increased specific action, quinotoxin could be administered in a very much reduced dosage as compared with quinine, then owing to the comparative simplicity of its preparation, it might well form a formidable rival to the natural alkaloids of commerce.

3. *In treatment of Pneumonia.*—Most of the work in this direction appears to have followed the 'side-chain theory,' and to have been carried on with ethyl hydrocupreine which was before the war manufactured in Germany and sold in small quantities on this market under the registered name of 'Optochin.' No work has, up to the present, been published to show whether a further increase in the side chain to the higher homologues renders this treatment more effective.

Apparently the results obtained up to August, 1918, do not show any marked superiority over the ordinary commercial alkaloids.

4. *As an Antiseptic in the treatment of Wounds.* —A considerable amount of work has been done in Germany on the use of the higher alkylated homologues of the hydrocupreine series as a wound treatment in war surgery. Prof. Klapp, following on the work of Morgenroth and Tugendreich (Pharm. Zeit. Nov. 7, 1917, 603 ; and Deut. Med. Woch. 1917, 44), claims that, by lengthening the side chain as far as the isoctyl member of the hydrocupreine series, he has obtained an antiseptic superior to any known wound dressing. He claims that this compound has 20 times the power of quinine, and 10 times that of ethyl-hydrocupreine, in the destruction of streptococci.

These comparative results are quoted as having been obtained 'in vitro,' and must therefore be accepted with reserve ; and time alone will show whether this treatment will really be found to be superior to the far simpler and cheaper Dakin's solution or the highly satisfactory 'chloramine-T' treatment.

Although the precise relation between the constitution of the alkaloids and their therapeutic value has clearly not been established, enough work has been done to indicate a possible future for derivatives of cinchona alkaloids either of the 'unsaturated' (quinotoxin) or of the 'increased side chain' type, which from the purely scientific and medical point of view, might be of even greater importance than the present universal use of the parent alkaloids as one of our few standard remedies.

General Properties of the Cinchona Alkaloids. —These bases are mostly white crystalline nonodorous bodies, with a bitter flavour and strong basic properties, some being sufficiently powerful to displace ammonia from its salts. On heating strongly they decompose, evolving fumes of a colour resembling iodine vapour, and with a quinolinic odour. They are very slightly soluble in water, but are fairly readily soluble in organic solvents, there being, however, notable exceptions. Acids dissolve these alkaloids forming two series of salts, neutral and acid, of the general types $B_2H_2SO_4$ and $B \cdot H_2SO_4$. Even more acid salts of the type $B \cdot 2H_2SO_4$ are

obtainable in some cases. These salts are generally white crystalline bodies, of very varying solubility in solvents generally, and with a very bitter taste. Solutions of the salts in water when treated with alkalis precipitate the alkaloid, with the exception of cupreine, which, being phenolic in character, is soluble in alkalis.

A strong blue fluorescent solution is obtained with many of these alkaloids when dissolved in dilute sulphuric acid, viz. quinine, quinidine, hydroquinine, hydroquinidine, diquinicine. This is a very delicate test which is best seen by reflected light. The haloid salts do not show this fluorescence, which is also destroyed by adding a haloid salt or hyposulphite to the sulphuric acid solution.

All the cinchona alkaloids have, in solution, a marked rotatory influence on polarised light, which is affected by the temperature of the solution, the solvent employed, the concentration, and the amount of acid present. With mineral acids the maximum rotation is observed when the acid is present in little more than the amount to form the acid salt ; but with organic acids a much greater amount of free acid is required.

When certain of these bases are treated in dilute solution with chlorine- or bromine-water, followed by ammonia added drop by drop, a deep green colouration or precipitate is obtained. This is known as the *thalleioquin* test *(thallos*, a young twig), and is given by quinine, quinidine, quinicine, hydroquinine, hydroquinidine, cupreine, and diquinicine.

The cinchona bases are di-tertiary amines forming mono- and di-alkyl iodide additive compounds.

The hydrochlorides of the bases form double compounds with several metallic chlorides, of which the chief are : (a) the chlorozincates of the general formula $B,2HCl,ZnCl_2$; (b) the chloromercurates $B,2HCl,HgCl_2$; (c) the chloroaurates $B,2HCl,AuCl_3$; (d) the platinochlorides, of which there are two types, $B,2HCl,PtCl_4$ and $B_2,2HCl,PtCl_4$. Of these (c) and (d) have been much used in the determination of the molecular weights of the bases.

The cinchona alkaloids are nearly completely precipitated from solution by tannic, picric, or phosphotungstic acid, potassium mercuric iodide (Mayer's reagent), and potassium bismuth iodide (Dragendorff's reagent).

Methods of Extracting the Alkaloids of Cinchona Barks.—Before extracting the bark it must be treated in such a manner as will ensure the alkaloids being in a suitable condition for extraction. For this purpose the bark must be in a finely powdered condition, the finer the powder the more rapid and thorough being the extraction. The *whole* of the bark should be ground to pass a sieve with at least forty meshes to the linear inch. This point is of special importance in assaying, as cases are known in which the harder portions of the bark (which might be rejected as gruffs if the whole were not finely ground) are richer in alkaloids than the softer parts. The next stage in the process is that of liberating the alkaloids from their combinations with the natural acids of the bark, in order to render them soluble in the solvent employed. This is effected by moistening the

bark with a dilute alkali, or by mixing it with lime and damping with water, and allowing to stand for some hours. The whole may then be dried, powdered, and extracted with chloroform, ether, petroleum spirit, or a mixture of these; or the damp bark may be extracted direct with petroleum, amyl alcohol, benzene, naphtha, or mixtures of these. Thus Landrin (Compt. rend. 1889, 108, 750) and Zebel (Chem. Zeit. 1891, 15, 735) describe processes using petroleum; the Brit. Pharm 1914, directs the use of a mixture of 3 volumes of benzene and 1 of amyl alcohol; while the U.S Pharm. 1916, employs a mixture of 2 volumes of ether and 1 volume of chloroform. On the large scale the solvent employed will naturally be the cheapest, while on the small scale, where an efficient reflux extraction apparatus can be used, chloroform or ether are convenient.

Zebel (l c.) describes the commercial process thus: The finely powdered bark is ground to a thin paste with lime, sodium hydroxide, or sodium carbonate, and extracted with warm paraffin oil. On standing the oil separates, when it is run off and shaken with sulphuric acid; this acid solution is boiled, and while boiling is neutralised (to litmus paper) with sodium carbonate and allowed to cool. Quinine sulphate crystallises out on cooling, while cinchonidine, cinchonine, and quinidine remain in solution as sulphates. The quinine sulphate is purified by recrystallisation from water after treating with animal charcoal. The mother-liquor containing the other alkaloids is treated with sodium hydroxide and the precipitate treated with dilute alcohol. Of the three bases precipitated, quinidine and cinchonidine are dissolved by the alcohol, while cinchonine is left behind; the two former can then be separated by means of their neutral tartrates, that of quinidine being considerably the more soluble.

Landrin (l c.) gives this description of the small scale extraction: 300 grams of bark are powdered and passed through a No 40 sieve, then mixed thoroughly with 1 litre of milk of soda-lime containing 75 grams of quicklime and 75 grams of solution of sodium hydroxide (sp gr. 1·375). To this mixture, diluted if necessary by adding a little water, 2 litres of petroleum are added, heated to 100° for 20 minutes, with constant agitation; the oil is then decanted, and the extraction repeated with a second 2 litres. The 4 litres of extract are washed twice with 75 c c. of 10 p c sulphuric acid added to 150 c c of water; and a third time with one-third of these quantities.

The British Pharmacopœia, 1914, method is as follows: 10 grams of the bark in No 60 powder are mixed with 6 grams of slaked lime, and the whole moistened with 22 c c. of water and allowed to stand for 2 hours. This is transferred to a flask provided with a reflux condenser and boiled with 130 c c of benzolated a'mylic alcohol (benzene, 3 volumes; amyl alcohol, 1 volume) during 30 minutes. The liquid is filtered off and the treatment repeated twice, the mixture of bark and lime being finally transferred to the filter and washed with the solvent till exhausted.

The U.S. Pharmacopœia (9th revision, 1916) process is: Introduce 5 grams of cinchona in No. 40 powder into a 500 c.c. flask, and add 200 c.c. of a mixture of chloroform and ether (1 : 2). Stopper the flask, shake it well, and let it stand 10 minutes. Then add 5 c.c. of ammonia water, shake the flask frequently for 1 hour, and let it stand from 8 to 10 hours. Now add 10 c c. of distilled water, shake the mixture thoroughly, and when the drug has settled decant 160 c.c. of the solution, representing 4 grams of cinchona. Filter through a pledget of purified cotton into a separator, and rinse both cylinder and cotton with ether. Completely extract the alkaloids from the chloroform-ether solution by shaking out repeatedly with weak sulphuric acid.

An older method of extracting the bark, due to de Vrij, was that of treating the powdered bark with a large excess of milk of lime, drying down and extracting with alcohol. But this has been entirely given up owing to the great amount of colouring matter extracted with the alkaloids, and the consequent difficulty in purification.

Assay of Cinchona Barks.—The accurate assay of a bark is much more difficult than appears at first sight owing to the obstinacy with which one alkaloid will form more or less definite compounds with the others when crystallising as alkaloid or salt, and also on account of the changes in its solubility in solvents when varying quantities of other alkaloids are present. For these reasons a process of assay giving good results when, for instance, a Ledger bark, in which quinine is the main constituent is tested, will not be accurate for a Succirubra bark in which the cinchonidine and cinchonine usually exceed the quinine in amount. A knowledge of the type of bark being assayed, and of its alkaloidal contents, is therefore of great importance, the experienced analyst being able to foretell the state of purity of his various precipitates and so regulate his analysis.

A 'full' analysis of a bark usually consists of the estimation of the quinine, quinidine, cinchonidine, cinchonine, and total amorphous alkaloids. To obtain satisfactory results a quantity of alkaloid of about 5 grams should be available. It is desirable to start the assay with the estimation of the total alkaloids, as the subsequent work is simplified by so doing and the result is a useful check on the estimation of the individual alkaloids. For this purpose it is only necessary to evaporate the extract obtained by any of the methods described under the previous heading to constant weight; or, in the case of the paraffin and sulphuric acid extraction, to make alkaline with sodium hydroxide, wash out with chloroform, and evaporate to dryness Dry to constant weight at 100° 110°. Having obtained the weight of total alkaloids, add 3 c.c. of 10 p.c. sulphuric acid for every gram of alkaloid, and warm on the steam-bath till completely dissolved. Then add 80 c c. of distilled water for every gram of alkaloid, boil, and while boiling neutralise exactly to litmus paper with dilute ammonia solution (10 p.c.). On cooling for 2 or 3 hours with occasional stirring practically the whole of the quinine will crystallise out as sulphate, owing to it being almost insoluble in ammonium sulphate solution. Filter through counterpoised filter papers on the filter-pump, press the crystals down well, pumping as dry as possible,

and following with two washes of cold water each about equal in volume to the bulk of the precipitate. The filter papers and crystals are now dried to constant weight at 100°. The weight of anhydrous quinine sulphate found multiplied by 1·18 gives the amount of rough hydrated quinine sulphate, or by 0·868 the amount of rough quinine alkaloid. This quinine sulphate is neither white nor pure, being usually contaminated with colouring matter and cinchonidine sulphate, and requires further treatment, for which *see* under 'Quinine Sulphate.' But with the present-day pure Ledgeriana barks the weight may be taken as representing the true amount of quinine sulphate, as in some thousands of analyses of this bark by the present writers the amount of quinine sulphate left in the mother liquor almost exactly compensates for the impurities in the crystals weighed. It is, however, a safeguard in all cases to test for any undue amount of cinchonidine as described under 'Quinine Sulphate.'

To the mother liquor and washings from the crystals add about 20 grams of Rochelle salt, dissolved in 30 c.c. of hot water, and stir occasionally during 2 or 3 hours. Cinchonidine is completely precipitated as tartrate. This is collected on counterpoised filter papers at the pump, washed with three lots of cold water each about equal in bulk to the precipitate, which is then dried and weighed. This weight multiplied by 0 797 gives the cinchonidine alkaloid. Should the bark contain very little cinchonidine, and no tartrate be obtained in the 3 hours' standing, it is best to leave the solution for a full 24 hours to ensure complete precipitation. The filtrate from the cinchonidine tartrate is now evaporated to one-half, half its volume of methylated spirit and 5 grams of neutral potassium iodide dissolved in 5 c c. of water are added, and the liquid left for at least 2 hours with frequent stirring. The quinidine hydriodide is filtered off at the pump on a counterpoised filter paper, washed with a little 50 p.c. methylated spirit, dried and weighed. 0 0008 gram is added to this weight for each 1 c.c. of filtrate and washings, which total multiplied by 0·7186 gives the quinidine alkaloid. The filtrate is made alkaline with sodium hydroxide and shaken with ether (free from alcohol) in a separator, the aqueous portion drawn off and twice again shaken with small quantities of ether, the ether extracts bulked, allowed to stand 1 hour, and the cinchonine filtered off on counterpoised papers at the pump, two small washes with ether being given. The cinchonine is dried and weighed, and to its weight is added 0·0027 gram for each 1 c.c. of filtrate and washings. The ether evaporated to dryness and constant weight gives the total amorphous alkaloids, from which should be subtracted the weights added on as corrections for quinidine and cinchonine.

The above method is made up of the best points of the many published methods of assay, and will be found to give good results in inexperienced hands. For other methods, *see* Allen's Commercial Organic Analysis, 1912, vol. vi. 490–495.

The British Pharmacopœia, 1914, specifies that the bark (C. succirubra) ' when used for official purposes other than the preparation of alkaloids or their salts, shall yield 5–6 p.c. of total alkaloids, of which not less than half shall consist of quinine and cinchonidine. The method used is that of extracting the amylated benzene solution of alkaloids (*see* above) with dilute hydrochloric acid, neutralising the acid solution with ammonia, and precipitating the quinine and cinchonidine together as tartrates by the addition of Rochelle salt. The remaining alkaloids are then precipitated from the filtrate by ammonia.

The United States Pharmacopœia, 1905, prescribes 5 p.c. of total alkaloids and 4 p.c. of ether-soluble alkaloids (*i.e.* quinine, quinidine. and cinchonidine). This is carried out by dividing the acid solution of the alkaloids into two equal portions, shaking one with ammonia and chloroform-ether mixture to obtain total alkaloids, and the other with ammonia and ether for ether-soluble alkaloids. The U.S.P., 1916, omits the ' ether-soluble alkaloid ' test.

The German Pharmacopœia (1910) method consists of estimating the total alkaloids by extracting the chloroform-ether mixture (1 : 3) with decinormal acid in excess, and titrating back the excess of acid over the neutral point with decinormal alkali, using alcoholic hæmatoxylin solution as indicator. 6 5 p.c. of total alkaloids are required.

Titration methods are liable to serious errors and cannot be recommended, but can be employed as useful rough checks on analysis. Generally speaking, the free alkaloids are neutral to phenol-phthalein, the neutral sulphates ($B_2 \cdot H_2SO_4$) are neutral to litmus, brazil wood, lacmoid, cochineal, and hæmatoxylin, but alkaline to methyl-orange, which roughly indicates the bisulphate point ($B \cdot H_2SO_4$) (Allen, Analyst, 1896, 21, 85 ; Farr and Wright, Pharm. J. 1894, 25, 124 ; Messner, Zeitsch. angew. Chem. 1903, 16, 444 ; Engelhardt and Jones, Pharm. J. 1910, 30, 236 ; Katz, Ber. Deut. pharm. Ges. 1910, 20, 316).

Oudemans (Annalen, 1876, 182, 33) has strongly recommended the polarimetric assay of the cinchona alkaloids, and a good deal of controversy has raged around the subject ; the majority of the evidence appears to be against the method, owing to the difficulty of obtaining the bases in a pure enough condition for accurate polarimetric reading (Hesse, Annalen, 1875, 176, 205 ; 1876, 182, 128 ; Koppeschar, Zeitsch. anal. Chem. 1885, 24, 362 ; Léger, J. Pharm. Chim. 1904, 19, 427).

Quinine and its Derivatives and Salts. —Quinine alkaloid is usually prepared by precipitating a solution of quinine hydrochloride with an alkali or ammonia, washing free from chloride and drying at a low temperature. The commercial article is a soft white granular odourless powder with micro-crystalline structure, and contains up to 11 p.c. H_2O (dihydrate). It crystallises from ethereal solution below 10° with $3H_2O$ (14·3 p.c. H_2O), but the ethereal solution evaporated gives a resinoid mass containing $1H_2O$ (most other cinchona alkaloids give crystalline residues from ether). Alcoholic or ammoniacal solutions deposit needles with $3H_2O$, which rapidly effloresce in the air above 15° giving a dihydrate. This is the composition of the commercial article, although most pharmacopœias require the trihydrate. The

trihydrate loses all its water over sulphuric acid,
It melts at 57°, and in estimating the moisture
it is therefore best to dry for some hours at
40°–50°, then gradually raise the temperature
to 100°. In this way no melting takes place,
and the dehydration is rapid. Other hydrates
containing 1, 8, and 9H_2O have been described.
Anhydrous pure quinine melts at 174·9°. It
is a strong base displacing ammonia from its
salts in hot solution, and neutralising the
strongest acids. The pure base has a bitter
taste, which develops slowly, the commercial
article is more bitter on account of the presence
of impurities which give more rapid solution.
Ammonium and calcium salts notably increase
the solubility of the alkaloid in water, while the
alkalis render it less soluble. The anhydrous
alkaloid is soluble in 1750 parts of water, in
3450 parts of potassium hydroxide (5 p.c.), and
in 1890 parts of ammonia (10 p.c.) at 25°C.
The trihydrate is soluble in 0·8 parts of alcohol,
1·1 parts of chloroform, 1·9 parts of ether,
212 parts of glycerin, and 166 parts of benzene
at 25°C. Quinine is lævorotatory, the trihydrate
having in 97 p.c. alcohol $[a]_D^{15} = -145\,2° + 0\,657c$.

The anhydrous alkaloid in ether has $[a]_D^{15}$
$= -158·7° + 1·911c$, where $c = 1\,5–6·0$.

The chief impurities likely to be met with
in the commercial article are chlorides and
sulphates of the alkalis or ammonia, lime salts,
hydroquinine, cinchonidine, and cinchonine
1 gram should dissolve in a mixture of 6 c.c.
absolute alcohol and 3 c.c. ether to give a solu-
tion remaining bright on cooling (absence of
cinchonidine and cinchonine, and inorganic
salts). Hydroquinine which is liable to occur
up to 2 p.c., may be tested for as given under
' Quinine Sulphate '

Quinine is distinguished from the other alka-
loids by its ready solubility in ether, fluorescent
solution in dilute sulphuric acid (detectable
to the extent of 1 part in 500,000), by the
thalleioquin test, its insoluble neutral sulphate,
tartrate and chromate, and by its rotation

The following are the more important
derivatives of quinine :—

Quitenine $C_{19}H_{22}O_4N_2$ or

$C_{17}H_{18}O\cdot OCH_3\cdot COOHN_2$
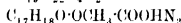
(Skraup, Annalen, 1879, 199, 348). This feeble
base, together with formic acid, is obtained
when quinine is oxidised with permanganate in
acid solution at 0°, and bears the same relation
to quinine as cinchotenine does to cinchonine
(see ' Constitution '). The quitenine is carried
down by the oxide of manganese, from which it
may be extracted with 40 p.c. alcohol On
concentration and filtration quitenine comes out
in rhombic prisms containing 4H_2O, slightly
soluble in water, insoluble in acids, but dissolves
in acids and alkalis. Quitenine is identical
with Kerner's dihydroxyquinine (Zeitsch. Chem.
1869, 5, 593). It gives the thalleioquin reaction,
and dissolves in dilute alcoholic sulphuric acid
with fluorescence. It is lævorotatory, giving
$[a]_D = -142°$; m.p. of anhydrous base 228°.
It gives a sulphate $B_3\cdot 2H_2SO_4,15H_2O$ in fine
needles. Heated with sulphuric acid it is
converted into an isomeric amorphous dark red
base, *quitenicine*, very soluble in water. Its

constitution is that of quinine in which the vinyl
is replaced by a carboxyl group. Heated with
hydriodic acid (sp.gr. 1·7) its methyl group is
eliminated, and a new base, *quitenol*, is obtained.

Quitenol $C_{17}H_{18}O\cdot OH\cdot COOH\cdot N_2$ crystal-
lises in fine needles containing 1H_2O, very
slightly soluble in water, alcohol, or ether.
It dissolves readily in acids and alkalis, being
precipitated from the latter by CO_2. It gives
the thalleioquin reaction, and a red colouration
in hydrochloric acid solution with ferric chloride.
Quitenol bears the same relation to quitenine,
that cupreine does to quinine (Bucher, Monatsh.
1893, 14, 598).

Quininic acid $C_9H_5\cdot OCH_3\cdot COOH$ N (6-meth-
oxy-4-carboxyquinoline). This acid is obtained
on oxidising quinine with chromic acid, being
the p-methoxy derivative of cinchoninic acid
derived from cinchonine under similar treat-
ment (Skraup, Ber. 1879, 12, 1104 ; Comstock
and Königs, Ber. 1884, 17, 1984 ; 1886, 19,
2853). It forms yellowish prisms, almost
insoluble in water, very soluble in acids and
alkaloids. It is slightly soluble in absolute
alcohol, giving a beautiful blue fluorescence,
which is destroyed by water or acids. Heated
with fuming hydrochloric acid under pressure it
loses its methyl group, yielding a phenolic body
xanthoquinine acid $C_9H_5\cdot OH\cdot COOH\cdot N$.

Meroquinene $C_8H_{10}\cdot CH : CH_2\cdot COOH\cdot NH$ (v.
' Constitution ' (Skraup, Monatsh. 1903, 24,
298)) This body forms small colourless needles,
m p 223°–224°, very soluble in water and acids,
almost insoluble in alcohol It is an interesting
example of a body in which the acidity of the
carboxyl group is neutralised by the alkaline
properties of the remainder of the molecule.
$[a]_D$ in 10 p.c. aqueous solution +27·9°. It
readily forms esters. On oxidation with chromic
acid it gives cincholoiponic and loiponic acids.

Cincholoiponic acid $C_8H_{10}(COOH),NH$. This
acid is derived from meroquinene by the oxida-
tion of the vinyl group It combines both with
acids and alkalis. It forms rhombic prisms
containing 1H_2O, melting at 126°–127°, and
when anhydrous, at 225°–226°. It is a dibasic
acid and a secondary base (Skraup, Monatsh.
1896, 17, 372 ; 1900, 21, 879). When the hydro-
chloride of this acid is heated with resorcin
and concentrated sulphuric acid, or zinc chloride,
a fluorescein is formed, which indicates that the
two carboxyls are in an ortho position to each
other (Müller and Rohde, Ber. 1894, 27, 1188).
A great deal of work has been done on the con-
stitution of this acid, for upon it depends the
proof of the constitution of the ' second ' half
of the molecule of the cinchona alkaloid. For
later work on its stereoisomerides, see Königs,
Ber. 1901, 34, 4336 ; Wohl, Ber. 1907, 40,
4693, 4711 ; 1909, 42, 627.

Loiponic acid $C_6H_8(COOH)_2NH$ (hexahydro-
pyridine-3 : 4-dicarboxylic acid) v. ' Constitution.'
Prismatic crystals, m.p. 259°–260°, fairly soluble
in water, easily soluble in alkalis and mineral
acids (Skraup, Monatsh. 1896, 17, 366).

Quinine chloride $C_{20}H_{23}ON_2Cl$. This body is
formed when dry quinine hydrochloride is
treated with phosphorus pentachloride in
chloroform solution, the hydroxyl group of the
quinine being replaced by chlorine. It has
basic properties, melts at 151°, gives the thalleio-
quin reaction, but does not fluoresce in acid

solution (Comstock and Königs, Ber. 1884, 17, 1984 ; 1885, 18, 1219 ; 1892, 25, 1545). On treatment with alcoholic potash hydrochloric acid is eliminated with the formation of quinene.

Quinene $C_{20}H_{22}ON_2,2H_2O$ forms large rhombic crystals melting at 81°–82°. On hydrolysis with 25 p.c. phosphoric acid it yields meroquinene and p-methoxylepidine (Königs, Ber. 1890, 23, 2669 ; 1894, 27, 900 ; 1895, 28, 3143 ; 1896, 29, 372). On heating with HBr (sp.gr. 1·49) quenene yields *apoquinene* (p-oxyapocmchene), thus :

$$C_{20}H_{22}ON_2 + HBr + H_2O$$
$$-- C_{19}H_{19}O_2N + CH_3Br + NH_3$$
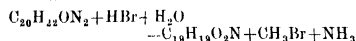
Apoquinene $C_{19}H_{19}O_2N$ forms crystals melting at 246°, very slightly soluble in water, benzene, · or ether, readily soluble in alcohol. Its solutions in sodium hydroxide or dilute hydrochloric acid are yellow (Königs and Comstock, Ber 1885, 18, 1226 ; 1886, 20, 2675).

Quininone $C_{20}H_{22}O_2N_2$ (p-methoxycinchonone) is obtained by carefully oxidising quinine (or quinidin) with chromic acid in the presence of acetic acid. Treated with nitrous acid it yields quinenic acid, and an oxime which splits up on hydrolysis into meroquinene and hydroxylamine (Rabe, Ber 1907, 40, 3655 . 1908, 41, 62 ; Annalen, 1909, 365, 353 ; 1910, 373, 85 ; 1911, 382, 365). Upon this hydrolysis Rabe has based his formula for the cinchona alkaloids (*see* p. 89).

Dihydroquinine $C_{20}H_{26}O_2N_2$. Schutzenberger (Annalen, 1858, 108, 348) obtained an oily body by the action of zinc and sulphuric acid on quinine, which he named dihydroquinine. This is not the dihydroquinine of commerce, *v.* Hydroquinine (Hesse, Ber 1882, 15, 854 ; Pum, Monatsh. 1895, 16, 72).

Tetrahydroquinine $C_{20}H_{28}O_2N_2$ is obtained by the action of sodium and alcohol on quinine (Lippmann and Fleissner, Monatsh 1895, 16, 630) ; also by electrolytic reduction (Freund and Bredenberg, Annalen, 1914, 407, 43).

Dichlorquinine $C_{20}H_{24}N_2O_2Cl_2$ is formed when quinine hydrochloride, dissolved in a mixture of acetic and hydrochloric acids, is treated with 1 molecule of chlorine. It is a colourless amorphous compound, melting at 97°, and closely resembles quinine in its chemical behaviour. Treated with alcoholic potash it loses 2HCl, yielding *dehydroquinine* $C_{20}H_{22}O_2N_2$. By the further action of chlorine on dichlorquinine, a tetra-chlorinated body $C_{19}H_{21}O_2N_2Cl_4$ is obtained (Christensen, Ber. Deut. pharm. Ges. 1915, 25, 256).

Hydroxychlorquinine $C_{20}H_{24}O_2N_2(ClOH)$ is obtained as an amorphous colourless powder, m.p. 110°, when quinine dissolved in cold dilute hydrochloric acid is treated with 1 molecule of chlorine dissolved in water (*ibid.*). When 3 molecules of chlorine are employed a tri-chlorinated body $C_{19}H_{21}O_3N_2Cl_3$ is obtained.

Tetrabromquinine $C_{20}H_{24}O_2N_2 \cdot Br_4$, obtained by treating quinine dissolved in sulphuric acid with excess of bromine-water. It is a yellow amorphous body with an odour of bromine.

Tribromquinine $C_{20}H_{24}O_2N_2,Br_3$, obtained by treating an alcoholic solution of tetrabromquinine with H_2S.

Dibromquinine $C_{20}H_{24}O_2N_2 \cdot Br_2 + 2H_2O$ is obtained from the mother liquor of tribromquinine by precipitation with ammonia. Another anhydrous dibromquinine is obtained by acting on a chloroform-alcohol solution of quinine hydrochloride with bromine dissolved in chloroform (Comstock and Königs, Ber. 1892, 25, 1500).

Iodoquinines. By the action of iodine dissolved in alcohol or potassium iodide many badly defined iodoquinines have been obtained, *e.g.* $4B \cdot 3I_2$, $4B \cdot 5I$, $B \cdot H1 \cdot I$, $B \cdot 2HI$, $B \cdot H1 \cdot I_4$ (Bauer, Arch. Pharm 1874, 5, 392).

Hydrochloroquinine $C_{20}H_{25}ClO_2N_2$, obtained by treating quinine at low temperature with HCl saturated at −17° ; m.p. 186°–187°. Insoluble in water, soluble in ether or methyl alcohol. It shows fluorescence and gives the thalleioquin reaction. Quinine is regenerated on treatment with alcoholic potash (Comstock and Königs, Ber. 1887, 20, 2510 ; 1892, 25, 1539). Hesse obtained this body by heating quinine with HCl (sp.gr. 1·189) at 85° (Annalen, 1868, 147, 241).

Hydrobromoquinine $C_{20}H_{25}BrO_2N_2$ is obtained by treating quinine hydrobromide with HBr saturated at 17°C. at a low temperature for 5 days. It is soluble in ether, but its sulphuric acid solution does not fluoresce (Comstock and Königs, Ber. 1896, 29, 803).

Hydroiodoquinine $C_{20}H_{25}IO_2N_2$, obtained by treating quinine with HI (sp.gr. 1·9) on the water-bath for 1 hour. Crystals melt at 150°–155°. Soluble in ether, from which crystals containing $I(C_2H_5)_2O$ are obtained. Its solution in sulphuric acid is fluorescent, and gives the thalleioquin test. Heated with alcoholic potash it yields a mixture of quinine, pseudoquinine, isoquinine, and niquine (Skraup, Monatsh. 1893, 14, 431, 446 ; Lippmann and Fleissner, *ibid.* 1891, 12, 327, 372 ; 1892, 13, 429 ; 1893, 14, 553).

Apoquinine $C_{19}H_{20}(OH)_2N_2$ is obtained by heating quinine under pressure to 145° with HI (sp.gr. 1 25–1·35). It is an isomeride of cupreine, which is also converted to apoquinine by heating under pressure with HCl (sp.gr. 1·125). It crystallises in large needles of m.p. 210°, and $[a]_D^{15} = -178 \cdot 1°$ for a 2 p.c. solution in 97 p.c. alcohol The acid oxalate $B_2 \cdot 3C_2H_2O_4$ and iodohydrate $B \cdot 2HI$ crystallise readily. It gives similar addition products to quinine with the haloid acids, hydroiodoapoquinine yielding on treatment with alcoholic potash the isomer *isoapoquinine* melting at 176° (Lippmann and Fleissner, Monatsh. 1891, 12, 332 ; 1893, 14, 553 ; 1895, 16, 33 ; Mauther, Ber. 1895, 28, 1972).

Derivatives Isomeric with Quinine.—**Niquine** $C_{19}H_{24}O_2N_2$ (*see* Hydroiodoquinine). This alkaloid behaves very similarly to quinine, forming similar salts, addition products, &c. Its sulphuric acid solution fluoresces, and it gives the thalleioquin reaction. It is soluble in alcohol, ether, chloroform, or benzene ; slightly soluble in boiling water, from which crystals containing $2H_2O$ are obtained ; $[a]_D = -129 \cdot 2°$ for a 1 p.c. solution in 98 p.c. alcohol (Skraup, Ber. 1892, 25, 2911 ; Monatsh. 1893, 14, 428 ; Lippmann and Fleissner, Monatsh. 1893, 14, 553). By treating the bihydriodide of hydroiodo-niquine with alcoholic potash niquine is

in part reformed together with an isomer isoniquine.

Isoniquine $C_{19}H_{24}O_2N_2$ crystallises from alcohol in the form of benzoic acid and melts at 208°–209°. It shows fluorescence in sulphuric acid, and gives the thalleioquin reaction (Skraup, Lippmann and Fleissner, *l.c.*).

Pseudoquinine $C_{20}H_{24}O_2N_2$, an isomer of quinine (*v.* hydriodoquinine), forms prisms melting at 190°–191°. It is not very soluble in ether, readily soluble in alcohol; $[\alpha]_D = -164.4°$ for a 1 p.c. solution in 98 p.c alcohol

Isoquinine $C_{20}H_{24}O_2N_2$, an isomer of quinine (*v.* hydroiodoquinine), crystallises in needles, melting at 185°–186°, and having $[\alpha]_D^{27} = 186.8°$ for 0.9 p.c. solution in 97 p.c alcohol It is readily soluble in ether and benzene, very slightly soluble in boiling water, and reacts generally like quinine (Skraup, Monatsh 1893, 15, 433; 1894, 16, 37). Hesse has also named a base isoquinine, which he obtained by the action of concentrated H_2SO_4 on quinine at 120°–130°, or by heating with glycerin at 180°–210° (Annalen, 1874, 174, 340; 1875, 178, 253, 1888, 243, 149; 1893, 276, 103).

Quinicine (quinotoxin) $C_{20}H_{24}O_2N_2$, an isomer of quinine, was first prepared by Pasteur in 1853 by heating quinine bisulphate with a little water at 160°, and afterwards isolated from quinine tails by Howard (Chem. Soc Trans. 1871, 24, 61; 1872, 25, 1011). It forms a reddish-yellow amorphous mass melting at about 50°, nearly insoluble in water, soluble in chloroform, ether, and alcohol, the latter solution rapidly absorbing CO_2 from the air It forms salts of which the oxalate $B \cdot C_2H_2O_4, 9H_2O$ bitartrate $B \cdot C_4H_6O_6, 6H_2O$, sulphocyanide

$$B \cdot HCNS, \tfrac{1}{2}H_2O$$
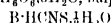
hydriodide $B \cdot HI, H_2O$, chloroplatinate

$$B \cdot H_2PtCl_6, 2H_2O$$
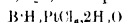
and aurichloride are crystalline. Hesse also obtained a crystalline sulphate $B_2 \cdot H_2SO_4, 8H_2O$. It is completely precipitated from its solutions by excess of potassium thiocyanate as an oil rapidly becoming crystalline. $[\alpha]_D^{15} = +44.1°$ for a 2 p.c. solution in $CHCl_3$. It gives the thalleioquin reaction, but does not show fluorescence in sulphuric acid solution. It is soluble in ammoniacal salt solutions, from which other extracts it (separation from other cinchona alkaloids). (Hesse, Annalen, 1875, 178, 213; Miller and Rohde, Ber. 1895, 28, 1058; Skraup, Monatsh. 1899, 20, 573; Howard and Chick, J. Soc. Chem. Ind. 1909, 28, 53; Pharm. J. 1917, 99, 143.)

Quinine Salts.—**Quinine sulphate**

$$B_2 \cdot H_2SO_4, 7\tfrac{1}{2}H_2O$$
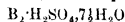
This salt occurs as white light silky needles, odourless, but with an intensely bitter taste. The hydration is rather indefinite, being recognised as $8H_2O$ by the French Pharmacopœia (=16.17 p.c.), $7\tfrac{1}{2}H_2O$ by the B.P. (=15.3 p.c.), and $7H_2O$ by the U.S.P. (=14.5 p.c.). It is completely dehydrated at 100°. Exposed to the air it loses water until $2H_2O$ remain (=4.8 p.c.), the same amount being absorbed if the fully exsiccated salt is exposed to moist air. The chemically pure salt crystallises in large heavy

needles, the lighter character of the commercial article being due to the presence of a little hydroquinine and cinchonidine, or by being crystallised slightly alkaline or from solutions containing ammonium sulphate. It is soluble in 740 parts of water at 15°, in 30 parts at 100°; in 65 parts of alcohol at 15°, in 6 parts at boiling-point; in 24 parts of glycerin at 15°, 1000 parts of chloroform at 15°; readily soluble (1 in 7) in a mixture of chloroform, 2 parts, absolute alcohol, 1 part The sulphates of the other cinchona bases and inorganic impurities are insoluble in this mixture, which is therefore a good test for the purity. It is much less soluble in water containing magnesium, sodium, or ammonium sulphate, but more soluble if calcium, sodium, or ammonium chloride, or potassium nitrate or chlorate be present. Quinine sulphate has $[\alpha]_D^{17} = -157.4°$ in absolute alcohol at a concentration of 2.2 p c of the $7\tfrac{1}{2}H_2O$ salt A 1 p c solution of the anhydrous sulphate in excess of dilute H_2SO_4 has $[\alpha]_D^{15} = 235°$. A dilute H_2SO_4 solution shows a strong blue fluorescence, detectable with about 1 part of quinine in 500,000. On treating a neutral solution of the sulphate in cold water with a slight excess of chlorine- or bromine-water added drop by drop, agitating for 20 seconds, and then adding ammonia drop by drop until faintly alkaline, a deep green colour is produced; or if more than 1 in 1000 of quinine is present a green precipitate is obtained (thalleioquin reaction) On neutralising the alkaline solution with dilute acid the colour changes to blue, which with more acid becomes red, reverting to green on again making alkaline. By a modified procedure Ramsden and Lipkin (Annals. Trop. Med 1918, 11, 443) are able to detect 1 part of quinine in 400,000. Neutral solutions of quinine sulphate in water give the following almost insoluble precipitates : with potassium chromate $B_2 \cdot H_2CrO_4, 2H_2O$, soluble 1 in 3150; with potassium oxalate

$$B_2, (C_2H_2O_4), 6H_2O$$
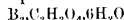
soluble 1 in 1400; with potassium picrate $B_2, C_6H_3N_3O_7$, soluble 1 in 3400; with sodium salicylate $B, C_7H_4O_3, H_2O$, soluble 1 in 2100; with tannic acid $B, (C_{14}H_{10}O_9)_3, 8H_2O$, soluble 1 in 2000; with Rochelle salt $B_2, C_4H_6O_6, H_2O$, soluble 1 in 950; all at 25°. These are the solubilities of the respective precipitates in water: the solubility is less in excess of the reagent.

On adding alcoholic iodine solution to an alcoholic solution of quinine acidified with sulphuric acid an iodosulphate of quinine $B_4(H_2SO_4)_2(HI)_2I_4, 6H_2O$, called after its discoverer, *Herepathite*, is thrown down as a reddish precipitate (Ann. Chim. Phys. 1854, 40, 249). It crystallises from strong alcohol in tabular crystals, green by reflected light, and red by transmitted light; almost insoluble in cold water or dilute alcohol, soluble 1 in 1000 of hot water, but much more soluble in acidified alcohol. By a special method of concentration, Ramsden and Lipkin have been enabled to identify as little as 1 part of quinine in 4,000,000 of urine, or in 20,000,000 of water by the herepathite reaction under the micropolariscope (Annals. Trop. Med. 1918, 11, 444). Jorgensen

(J. pr. Chem. 3, 145; 14, 213, 256; 15, 65) has prepared whole series of salts similar to herepathite, having varying quantities of acid, iodine, and water.

Most of the above-mentioned insoluble salts have been proposed as means for the estimation of quinine in mixtures of the cinchona alkaloids, but none have stood the test of time on account of the separations not being at all perfect, others of the alkaloids being co-precipitated.

Estimation.—Two classes of products will be dealt with here . (*a*) the rough quinine sulphate obtained as described under ' Assay of Cinchona Barks,' and (*b*) commercial quinine sulphate. The only alkaloidal impurities likely to occur in either are cinchonidine and hydroquinine. Of these two, hydroquinine is easily and rapidly estimated, but the estimation of cinchonidine is a much more difficult matter. For instance, it might be thought that advantage might be taken of the different solubilities of quinine sulphate (1 in 740) and cinchonidine sulphate (1 in 92) in water at 15°. But it is found that on dissolving a quinine sulphate containing cinchonidine in water at 100°, and allowing the solution to cool to 15°, the majority of the cinchonidine will crystallise out again with the quinine. As many as four recrystallisations will be necessary to remove the whole of the cinchonidine from the quinine. If now the mother liquors be combined and evaporated to dryness on the steam-bath a product is obtained containing about one-fifth of the original quinine together with all its impurities. If this salt be now shaken into purified ether and aqueous ammonia (sp.gr. 0·959) and cooled down to 0° for 24 hours, most of the cinchonidine will crystallise out at the layer of the two liquids, and may be filtered off, dried, and weighed. A modified form of this test, due to Prunier (J. Pharm. Chim. 1891, [v.] 23, 163 and 265), was the official method of the B.P. 1898, but being a very tedious process is no longer employed. Another method consists in precipitating a neutral solution of the quinine sulphate with Rochelle salt, drying and weighing the combined quinine and cinchonidine tartrates, and taking the polarimetric reading. This is still employed in some laboratories, and usually gives fairly accurate results in experienced hands. But it must be remembered that as the optical relations of the alkaloids are so diverse that should even a small percentage of hydroquinine tartrate be co-precipitated it will lead to inaccurate results. The temperature of the reading is also very important, as well as the concentration of the solution (Oudemans, Annalen, 1876, 182, 33; Hesse, *ibid.* 128; Koppeschar, Zeitsch. anal. Chem. 1885, 24, 362; Hooper, Pharm. J. 1886, 17, 61; Jungfleisch, J. Pharm. Chim. 1887, 15, 5; Léger, *ibid.* 1904, 19, 427; Montemartini and Bovini, Gazz. chim. ital. 1916, 46, 153).

De Vrij proposed a method of precipitating the quinine as neutral chromate (Arch. Pharm. 1887, 24, 1073), which was severely criticised by Hesse (Pharm. J. 1887, 17, 585, 665; *see* also Paul, *ibid.* 585, footnote).

Schaefer (Arch. Pharm. 1887, 25, 64) proposed a separation by means of the insoluble neutral oxalate of quinine, but the separation is not complete.

A better method is that proposed by De Vrij (Chem. Zeit. 1885, 968), and recommended by Hesse (Pharm. J. 1886, 17, 486) and D. Howard (Pharm. J. 1896, 3, 505), which takes advantage of the fact that when 5 grams of quinine sulphate are dissolved in 12 c.c., of $N/1H_2SO_4$, and allowed to crystallise, 80–90 p.c. of the quinine crystallises out as bisulphate, the whole of the cinchonidine remaining in the mother liquor. The crystal is filter-pumped and washed with 3 c.c. of cold water, and the filtrate shaken into 16 c.c. ether (sp.gr. 0·721–0·728) and 3 c c. of ammonia (sp.gr. 0·959), and left to stand for 24 hours, preferably at 0°. The cinchonidine crystallises out and may be filtered off, washed with a little water saturated with ether, dried, and weighed. Hesse points out that this cinchonidine is not pure, but consists of a double compound of quinine and cinchonidine $(C_{20}H_{24}O_2N_2\cdot2C_{19}H_{22}ON_2)$; and a portion of the cinchonidine is also soluble in the ethereal quinine liquor, these errors almost exactly compensating each other (Howard, *l.c.*). However, should quite accurate results be desired, the process may be modified by evaporating the first bisulphate mother liquor until it will again crystallise (sp gr. 1·100), filter-pump the crystals and wash as before, and shake this more concentrated cinchonidine liquor into ether and ammonia solution. The impure cinchonidine obtained is dried and weighed, then dissolved in hot absolute alcohol, and 2·1 c.c. of 50 p.c. H_2SO_4 added for each gram, and allowed to cool and stand, when the cinchonidine crystallises out entirely as tetrasulphate. This is filtered off on the pump, washed with a little alcohol, dissolved in water, precipitated with sodium hydroxide, filtered, washed with water, dried, and weighed as alkaloid. The alcohol mother liquor is diluted with water, the alcohol evaporated off on the water-bath, the two lots of bisulphate crystals added, and the solution diluted and neutralised with ammonia, when, on cooling, the pure quinine sulphate crystallises out and may be filtered off, dried, and weighed.

For rough quinine sulphate products (*a*) it is best to dissolve them in 40 times their weight of boiling water in a flask, add 10 p.c. of animal black and a few drops of dilute sulphuric acid, boil for 20 minutes, filter, and allow to crystallise. Filter off the quinine sulphate and return the mother liquor to the flask, together with the filter-paper and animal black; boil for 20 minutes, filter at the pump, wash the filter-paper with two or three lots of boiling water, evaporate down to about one-sixth of its bulk and neutralise with ammonia to litmus paper. Allow to cool and crystallise, filter off the quinine sulphate, and add this to the first crystals. Dry and weigh the decolourised quinine sulphate. This should then be put through one of the tests for cinchonidine given above, for preference De Vrij's bisulphate test. The mother liquor from the decolourised sulphate is added to the mother liquor from which the original impure sulphate was obtained, and is put through tests for other alkaloids described under the ' Assay of Cinchona Barks.' It should be noted here that neutral quinine sulphate is absorbed from its solutions by animal black (up to 15 p.c. of the weight of black used), and for that reason ' blacking ' in neutral solution is not permissible.

For commercial quinine sulphates (b) similar methods to the above may be employed, but as no (or infinitesimal) colouring matter is present the first decolourising process is not required. But as the above methods take considerable time to carry out the pharmacopœias adopt a qualitative test, in various forms, suggested by Kerner (Zeitsch. anal. Chem. 1862, 150; Arch. Pharm. 1878, 14, 438; ibid. 1887, 25, 712, 749). This test depends upon the fact that quinine sulphate is the least soluble of the sulphates of the cinchona bases; and that quinine is the most soluble of the common bases in dilute ammonia. When 2 grams of pure quinine sulphate is shaken with 20 c.c. of water at 60° for some time, and then cooled to 15° for at least half an hour (to prevent supersaturation), it gives a filtrate which precipitates with aqueous ammonia (sp.gr. 0·959), the precipitate just redissolving when 4·3 c.c. ammonia have been added. Now, quinine sulphate containing any of the other cinchona sulphates when treated in this manner takes more ammonia to give a clear solution; and by this means some idea of the purity of the quinine sulphate is obtained. This test has been universally adopted by the pharmacopœias, to which reference should be made for full details, as the directions vary in the different pharmacopœias. Quinine sulphate containing about 5 p.c. total of cinchonidine and hydroquinine sulphates will require between 6 and 7 c.c. of ammonia, while one containing about 10 p.c. of these impurities will require about 10 c.c. Points to be noticed in applying the test are that the weights of quinine sulphate and water taken do not, within reasonable limits, affect the result; the solution should be cooled gradually to 15° (never below), and retained at that temperature for not less than 30 minutes; the filtration should be rapid and the mixing very carefully done by gently rotating and tilting the testing tube, otherwise clotting of the precipitate may take place and a false result obtained. This test is greatly influenced should the quinine sulphate have an alkaline reaction (presence of free quinine), when the result is much in excess of that required for a neutral sulphate of the same degree of purity (D. Howard, Pharm J. 1896, iv. 3, 505); and also by the presence of alkaline sulphates, which make it appear purer than it is (Tutin, Pharm. J. 1909, iv. 29, 606). These points should be ascertained by testing the filtrate for neutrality with litmus paper; and by evaporating 5 c.c. to dryness and constant weight, when the residue should not weigh more than 0·008 gram, showing the absence of soluble inorganic salts (Bigmelli, Monit. Scient. 1908, 22, 175). Should the cooling of the mixture be carried out above 15° a larger amount of ammonia will be required, and between 15° and 20° a correction of 0·5 c.c. of ammonia for each degree above 15° may be applied. ·

Hydroquinine is best tested for by dissolving the quinine sulphate in dilute H_2SO_4, cooling to 0°, and adding 4 p.c. permanganate solution with constant stirring, so long as it is rapidly decolourised. The solution is then warmed, the coagulated manganese dioxide filtered off, the filtrate made alkaline with ammonia and shaken out with ether. The ether solution filtered and dried to constant weight will give the amount of hydroquinine present.

Quinidine, cinchonine, and amorphous alkaloid, which are seldom met with except in very rough quinine sulphate, are best estimated by recrystallising the salt and putting the mother liquor through the process given under the 'Assay of Cinchona Barks.'

Cupreine, never present now in commercial barks, may be estimated by shaking the recrystallised quinine sulphate into ether and sodium hydroxide, running off the aqueous portion, and washing it twice with more ether. The aqueous liquor is then run into a basin, acidified with sulphuric acid, and neutralised with ammonia On cooling any cupreine sulphate present crystallises out.

For the estimation and examination of quinine sulphate, see Hille, Arch. Pharm. 1903, 241, 54; and Lenz, Zeitsch. anal. Chem. 1888, 27, 549.

Kerner's test is recommended also for the other salts of quinine by all the pharmacopœias, but Tutin (l.c) has pointed out that the results obtained are quite useless, this is confirmed by the present writers' experience. The best method of examination of quinine salts, other than sulphate, is that of obtaining the alkaloid by putting through ether and ammonia, and following the procedure given under 'Assay of Cinchona Barks.'

Quinine disulphate $B \cdot H_2SO_4, 7H_2O$ crystallises out in white rhombic prisms when the normal sulphate is dissolved in an equivalent of 5 p.c. H_2SO_4. The salt effloresces readily, losing $6H_2O$ over sulphuric acid, and becoming anhydrous at 100°. When fully hydrated the salt softens at 90°, and as it melts gradually decomposes into quinine bisulphate (Howard and Chick, Pharm. J 1917, 99, 143). The dehydrated salt melts at 160°. It has an intensely bitter taste and the aqueous solution is strongly fluorescent. It is soluble in 10 parts of water and in 45 parts of alcohol at 15°; in 18 parts of glycerin, 920 parts of chloroform, and in 1770 parts of ether at 25°; in 1 part of water, and 0·5 part of alcohol at 60°. On exposure to light it turns yellow to brown on the surface of the crystals. This salt is usually very pure on account of the bi-sulphates of the other bases being much more soluble.

Quinine tetrasulphate $B2H_2SO_4, 7H_2O$ is obtained by dissolving the bisulphate in excess of strong sulphuric acid and concentrating over H_2SO_4. It is very soluble in water, less so in alcohol (Hesse, Annalen, 1873, 166, 222).

Quinine hydrochloride $B \cdot HCl, 2H_2O$ is obtained by decomposing a solution of quinine sulphate with barium chloride. It forms long needles, which become anhydrous at 100°, and melt at 158°–160° without decomposition. The commercial salt contains about 8 p.c. H_2O, and is usually very pure. It is soluble in 40 parts of water, in 9 parts of chloroform, and in 3 parts of alcohol at 15°; in 1 part of boiling water or 90 p.c. alcohol. It is largely replacing the sulphate in medicine on account of its superior solubility.

Quinine dihydrochloride $B \cdot 2HCl$, made by adding an equivalent of hydrochloric acid to the normal hydrochloride and carefully drying. It is a white crystalline powder containing

2-3 p.c. H₂O. Soluble in 0·75 part of water, 5 parts of alcohol, or 7 parts of chloroform, at 15°; insoluble in ether.

Quinine hydrobromide B·HBr,H₂O, made similarly to the hydrochloride, or by dissolving quinine alkaloid in one equivalent of HBr. Long white silky needles, soluble in 50 parts of water, 7 parts of alcohol, or 10 parts of chloroform at 15°; in 1 part of boiling water. It fuses at 152°, melting completely at 200°.

Quinine dihydrobromide H·2HBr,3H₂O, made by adding one equivalent of HBr to the normal hydrobromide. Large yellowish prisms, melting at 81°–82°, and soluble in 7 parts of water at 15°. Very soluble in hot water or alcohol, insoluble in ether.

Other salts of quinine in use, with their solubilities in water, and the amount of alkaloid they contain are :—

Acetate B·C·H₃COOH, 1 in 30 at 15° (84·4 p.c.); arsenate B₂H₃AsO₄,8H₂O, 1 in 650 at 25° (69·4 p.c.); bi-arsenate B·H₃AsO₄,2H₂O (64·5 p.c.); arsenite B₂·H₃AsO₃,4H₂O, 1 in 150 hot (83·1 p.c.); arrhenalate B₂·AsCH₃O (86·4 p.c.); arsanilate (p-amidophenylarsenate) B·NH₂·C₆H₄·AsO₃H, 1 in 635 at 15° (61·8 p.c.); benzoate B·C₇H₆O₂, 1 in 350 at 25° (72·6 p.c.), bimurcarbamide B·CO(NH₂)₂·2HCl,5H₂O, 1 in 1 at 15° (59·3 p.c.); camphorate

B₂·C₁₀H₁₆O₄,4H₂O,
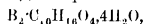
insoluble (70·4 p.c.); carbonate B·H₂CO₃,H₂O, soluble (73·7 p.c.); carbolate B·C₆H₅OH (77·5 p.c.); chlorate (B·HClO₃)₄,7H₂O (73·6 p.c.); chloromercurate B·2HCl·HgCl₂ (48·5 p.c.), chloroplatinate B₂·H₂PtCl₆,3H₂O (58·3 p.c.); bichloroplatinate B·H₂PtCl₆,H₂O (43·1 p.c.); chromate B₂·H₂CrO₄,2H₂O, 1 in 3150 at 25°, (80·8 p.c.); bichromate B·H₂CrO₄,8H₂O (55·3 p.c.); cinnamate B·C₉H₈O₂ (68·6 p.c.); citrate (basic) B₂·C₆H₈O₇,3H₂O, 1 in 1200 at 15° (72·5 p.c.); citrate (neutral) B₃(C₆H₅O₇)₂, 1 in 890 at 17° (71·7 p.c.); citrate (acid) B·C₆H₈O₇, 1 in 640 at 17° (62·8 p.c.); ethylsulphate B·H·C₂H₅SO₄ (71·2 p.c.); bi-ethylsulphate B·(H·C₂H₅·SO₄)₂ (56·2 p.c.); formate (quinoform) B·CH₂O₂,H₂O, 1 in 19 at 15° (83·5 p.c.); bi-formate B·(CH₂O₂)₂ (77·9 p.c.); glycerophosphate ('Kineurine')

B₂·C₃H₇O₃·H₂PO₄,4H₂O
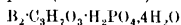
1 in 850 at 25° (72·6 p.c.); bi-glycerophosphate B·C₃H₇O₃·H₂PO₄,10H₂O (46·8 p.c.); hydrochlorophosphate B·HCl·(H₃PO₄)₂,3H₂O, 1 in 2 at 15° (53·0 p.c.); hydrochlorosulphate

B₂·2HCl·H₂SO₄,3H₂O
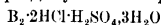
1 in 2 at 15° (74·4 p.c.); hydrofluoride B·HF (insoluble) (94·2 p.c.); hydriodide B·HI, 1 in 205 at 25° (71·7 p.c.); bi-hydriodide B·2HI,5H₂O 1 in 20 at 15° (48·4 p.c.); hypophosphite B·H₃PO₂, 1 in 250 at 15° (83·1 p.c.); isobutyl-formate B·C₅H₁₀O₂ (76·1 p.c.); isovalerianate B·C₅H₁₀O₂ (76·1 p.c.); lactate B·C₃H₆O₃, 1 in 6 at 15° (78·3 p.c.); methylsulphate B·HCH₃SO₄ (74·3 p.c.); nitrate B·HNO₃,H₂O, 1 in 70 at 25° (80·0 p.c.); oxalate B₂·C₂H₂O₄,6H₂O, 1 in 1400 at 25° (76·6 p.c.); binoxalate

B·C₂H₂O₄,H₂O
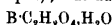
(75·0 p.c.); perchlorate B·2HClO₄,7H₂O (49·8 p.c.); periodide B·HI₃ (insoluble) (45·9 p.c.); **phosphate** B₂·H₃PO₄,8H₂O, 1 in 800 at 25°

(72·8 p.c.); quinate B·C₇H₁₂O₆,2H₂O, 1 in 7 at 15° (58·7 p.c.); salicylate B·C₇H₆O₃, 1 in 230 at 15° (70·2 p.c.); bi-salicylate B(C₇H₆O₃)₂,2½H₂O (50·2 p.c.); acetylsalicylate (aspirin-quinine or ' xaxaquin ') B·C₆H₄·OCO·CH₃COOH, 1 in 33 at 15° (64·3 p.c.); dibromsalicylate (' bromo-chinal ') B·C₇H₄O₃Br₂ (52·3 p.c.); succinate B₂·C₄H₆O₄,8H₂O (71·2 p.c.); sulphocyanide B·HCNS,H₂O (80·8 p.c.); bi-sulphocyanide B·2HCNS,½H₂O (71·8 p.c.); tannate (very varied composition), about 1 in 2000 at 15°; (20–30 p.c.); tartrate B₂·C₄H₆O₆,H₂O, 1 in 1000 at 15° (79·4 p.c.); bitartrate B·C₄H₆O₆,H₂O (65·8 p.c.); urethane-hydrochloride

B·(C₃H₇O₂NH₂)₂·HCl
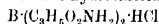
very soluble (60·1 p·c); valerianate

B·C₅H₁₀O₂,H₂O
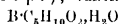
1 in 120 at 15° (73·0 p.c.). There are three general methods employed in making quinine salts : (1) to decompose an aqueous solution of quinine sulphate with the barium salt of the acid ; (2) to dissolve quinine alkaloid in a dilute aqueous solution of the acid ; and (3) to dissolve quinine alkaloid and the acid in separate portions of an organic solvent by heating, mix the solutions, and allow to cool and crystallise, or evaporate off the solvent.

Quinine Esters.—The following esters of quinine are also in use :—

Acetylquinine C₂₀H₂₃O₂N₂·COCH₃, made by heating quinine alkaloid with acetic anhydride at 60°–80° for several hours. The product is diluted with water, precipitated with ammonia, the acetylquinine collected, dried, and recrystallised from petroleum ether; m.p. 116°–117°.

Anisylquinine

C₂₀H₂₃ON₂—O—CO·C₆H₄·OCH₃
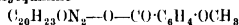
made by heating quinine alkaloid with phenyl-anisate at 120°–130° for several hours. The warm melted mass is treated with benzene and the free phenol removed with dilute NaOH. The ester is shaken out with dilute acid. Fine white needles. M.p. 87°–88°.

Benzoyl-quinine C₂₀H₂₃ON₂·O·CO·C₆H₅,made in a similar way to the above, by heating together quinine alkaloid and phenyl benzoate for several hours at 130°–140°.
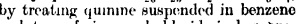
Cinnamyl-quinine C₂₀H₂₃ON₂·O·COC₉H₇, made by treating quinine suspended in benzene with a solution of cinnamyl chloride in benzene. Tasteless needles, soluble in hot, sparingly soluble in cold, water. M.p. 235°–236°.

Diquinine carbonate ('Aristoquinine')

(C₂₀H₂₃ON₂·O)₂CO
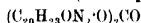
made by adding quinine alkaloid to a solution of phosgene in benzol, washing the resulting mass with water, and recrystallising the rough aristoquinine from alcohol. It forms crystalline groups of needles of m.p. 189°. It is an important ester on account of its tastelessness and its high percentage of quinine – 96·1 p.c.

Quinine ethyl carbonate (Euquinine)

C₂₀H₂₃ON₂O,CO·OC₂H₅
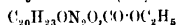
is similarly made by adding quinine to a benzol solution of ethylchloroformic ester. It occurs as white needles, tasteless; m.p. 95°. Easily soluble in alcohol, ether, and chloroform, not in water. It gives the thalleioquin reaction and fluoresces in dilute H₂SO₄. It forms similar

salts to quinine, but does not give the herepathite reaction. Its salicylate, a white tasteless crystalline powder, m.p. 195°, is the only commercial salt.

Salicylquinine (' Saloquinine ')

$C_{20}H_{23}ON_2 \cdot O \cdot COC_6H_4OH$

made by heating quinine salicylate with salol for several hours at 140°–150°. It crystallises from ether in large colourless crystals insoluble in water; m.p. 140°. Its salicylate is known as ' Rheumatine.'

Quinine carbophenetidide (' Chinaphenine ') $C_{20}H_{23}ON_2 \cdot O \cdot CO \, NHC_6H_4OC_2H_5$ occurs as a white tasteless powder, slightly soluble in water, easily soluble in organic solvents.

Hydroquinine, its derivatives and salts.

Hydroquinine $C_{20}H_{26}O_2N_2$ is invariably present in commercial quinine sulphate to the extent of 1–2 p.c. It may be prepared (and estimated) by converting the quinine sulphate into bisulphate by the addition of 12 c.c. of N/1 H_2SO_4 for each 5 grams of salt taken, filtering off the crystals, evaporating the mother liquor again to crystallising-point, filtering off the second crystals, adding ice to the mother liquor till cooled to 0° and then adding ice-cold permanganate solution drop by drop with constant stirring until the colour of the permanganate is no longer rapidly discharged. The liquor is now warmed until the manganese oxide coagulates, when it is filtered and shaken with ammonia and ether. The aqueous portion is given two more washes with ether, and the ethereal solutions bulked and evaporated to dryness, the hydroquinine alkaloid being obtained as a pale yellow crystalline mass.

Commercially, hydroquinine is now prepared by the hydrogenisation of quinine sulphate in dilute acid solution in the presence of (a) spongy metals of the platinum group (D R. P. 252136, 1912); (b) palladium black (Eng Pat 3948, 1912); (c) palladium coated on barium sulphate (D. R. P. 234137, 1911); or (d) by the action of 2 p.c. formic acid in the presence of palladium (D. R. P. 267306, 1913) In the last process the formic acid decomposes into carbon dioxide, which escapes, and hydrogen, which enters the quinine molecule at the vinyl group.

Hydroquinine crystallises in fine anhydrous needles from chloroform or ether, readily soluble in most organic solvents, sparingly in water, but more soluble in dilute ammonia, $[a]_D^{20°} = -142 \cdot 2°$ in 95 p.c. alcohol ($c=2 \cdot 4$ p.c.), m.p. 172°. In physical and chemical properties it closely resembles quinine, forming similar crystalline salts of like solubility.

The *chief salts of hydroquinine* are : acetate $B \cdot C_2H_4O_2, 5H_2O$, needles, soluble in water and alcohol; arsenate $B_2 \cdot H_3AsO_4, 10H_2O$; benzoate $B \cdot C_7H_6O_2$, soluble in alcohol; chromate $B_2 \cdot H_2CrO_4, 6H_2O$, yellow needles, soluble 1 in 663 of water at 15°; citrate $B_2 \cdot C_6H_8O_7, 10H_2O$, sparingly soluble in water; hydrobromide $B \cdot HBr, 2H_2O$, needles, freely soluble in water; dihydrobromide $B \cdot 2HBr, 3H_2O$, needles, very soluble in water; hydrochloride $B \cdot HCl, 2H_2O$, long flat prisms, freely soluble in water and alcohol; dihydrochloride $B \cdot 2HCl$, very soluble in water; herepathite, $4B \cdot 3H_2SO_4 \cdot 2HI \cdot I_4, 6H_2O$,

insoluble; hydriodide $B \cdot HI$, amorphous, freely soluble in water; dihydriodide $B \cdot 2HI, 4H_2O$, yellow crystals, soluble in hot water; iodohydriodide $B \cdot 2HI \cdot I_4$, dichroic needles; hyposulphite $B_2 \cdot H_2S_2O_3, 2H_2O$, small prisms, sparingly soluble in water; oxalate $B_2 \cdot C_2H_2O_4, 6H_2O$, sparingly soluble in water; phosphate $B_2 H_3PO_4, 7H_2O$, needles, sparingly soluble in water; platinochloride $B_2 \cdot H_2PtCl_6, 3H_2O$, amorphous, sparingly soluble in water; diplatinochloride $B \cdot H_2PtCl_6, 2H_2O$, amorphous, sparingly soluble in water; salicylate $B \, C_7H_6O_3$, needles, soluble in alcohol; sulphate $B_2 \, H_2SO_4$, 6 or $8H_2O$, needles, soluble in 348 of water at 15°; disulphate $B \, H_2SO_4, 3H_2O$, long thin needles, very soluble in water; tetrasulphate $B \cdot 2H_2SO_4$, amorphous, very soluble in water; tartrate $B_2 \cdot C_4H_6O_6, 2H_2O$, prisms, soluble in 545 parts of water at 17°.

Hydroquinine unites with 1 molecule of cupreine, quinidine, or hydroquinidine, and with 2 and 3 molecules of cinchonidine or hydrocinchonidine to form crystalline compounds (Hesse, Ber 1882, 15, 854; Annalen, 1887, 241, 255; Pum, Monatsh. 1895, 16, 72).

Hydroquinicine. On heating hydroquinine disulphate to 140° it is converted into its isomer hydroquinicine. The pure base is obtained by pouring the melted mass into water, and shaking the solution with NaOH and ether. The residue left on evaporation when dissolved in alcohol and neutralised with H_2SO_4 yields the crystalline sulphate, which is filtered off from the thick brown mother liquor and re-crystallised to give the pure salt, in delicate acicular colourless needles readily soluble in water and in alcohol. A solution of the sulphate in water is pale yellow, which on acidification assumes an intense yellowish-green colour. Alkaline hydroxides precipitate the free alkaloid as a resinoid mass which gradually dissolves in ammonia or ammonium salts solutions, but not in the fixed alkalis. The hydrochloride is amorphous and gives $[a]_D^{15°} = -17°$, $c=3$ in excess of dilute HCl. It yields a platinochloride $B \cdot H_2PtCl_6, H_2O$, as a pale-yellow flocculent precipitate changing to orange-coloured crystals, insoluble in water and sparingly soluble in dilute HCl. An ethereal solution of oxalic acid produces in an ethereal solution of the alkaloid an amorphous brown precipitate, soluble in chloroform. This distinguishes it from quinicine, which yields a voluminous precipitate of minute needles under similar conditions.

Hydrocupreine $C_{19}H_{24}O_2N_2$ is derived from hydroquinine by heating it with 8 parts of HCl (sp.gr. 1·125) at 150° in sealed tubes. The unchanged hydroquinine is removed by shaking the acid solution with NaOH and ether, the hydrocupreine being obtained as sulphate by neutralising the alkaline layer with dilute H_2SO_4. The free alkaloid forms a crystalline powder $C_{19}H_{24}O_2N_2, 2H_2O$, freely soluble in organic solvents, slightly soluble in ammonia. It melts at 168°–170°, is strongly basic, forming crystalline salts, but is also phenolic, dissolving in alkalis. Its sulphate $B_2 \cdot H_2SO_4$ is sparingly soluble in water and in alcohol, the dihydrochloride $B \cdot 2HCl, H_2O$ being freely soluble. It forms a sparingly soluble crystalline **tartrate**

$B_2 \cdot C_4H_6O_6,2H_2O$, and an orange-red crystalline platinochloride $B \cdot H_2PtCl_3$, insoluble in water and dilute HCl. Hydrocupreine is important as it is the source of the alkyl-hydrocupreïnes of which ethyl-hydrocupreïne hydrochloride $C_{21}H_{26}O_2N_2 \cdot HCl$ (*optochin*) has been tried recently as a specific for pneumonia (Morgenroth, Berl. Klin. Woch. 1911, 34. 44; *ibid.* 1914, 47–48; Sir Almroth Wright, Lancet, 1912, 1633, 1705; Pyman, Chem. Soc. Trans. 1917, 662, 1127); and the isoctyl derivatives as a wound disinfectant (Morgenroth and Tugendreich, Biochem. Zeitsch 1917, 79, 257; Schaeffer, *ibid.* 1917, 83, 269; Bieling, *ibid.* 1918, 85, 188).

Ethyl-hydrocupreïne hydrochloride occurs as a white crystalline powder, m.p. 242°, soluble in 10 parts of water, giving a blue fluorescence with dilute H_2SO_4, and having a bitter flavour. Soluble in 90 p.c. alcohol. The free alkaloid is precipitated by NaOH, and is soluble in chloroform.

The hydrochlorides of the higher alkyl-hydrocupreïnes are insoluble in water, the dihydrochlorides, which are soluble in 30–40 parts of water, being the salts prepared for use **Iso-octyl-hydrocupreïne dihydrochloride** ('Vuzin') occurs as a greenish-yellow amorphous powder giving a milky solution in 30–40 parts of water, which at higher dilution is merely opalescent.

Quinidine, its Derivatives and Salts —**Quinidine** (originally called 'conquinine') ($C_{20}H_{24}O_2N_2$), the only known natural stereo-isomer of quinine, occurs in most cinchona barks, especially C. pitayensis, and also in cuprea bark It was not prepared commercially at one time, but was precipitated with the amorphous alkaloids in the quinine tails, the whole being termed 'quinoidine' This was then a convenient source of quinidine, which could be extracted from the powdered quinoidine by means of ether (Hesse, Annalen, 1868, 146, 357; 1873, 166, 232). However, quinidine is now extracted and purified on the commercial scale, only a small amount being precipitated with the amorphous quinoidine It is most conveniently isolated from the quinine mother liquor as hydriodide, as given under the 'Assay of Cinchona Barks,' being the least soluble of the cinchona hydriodides in neutral aqueous solution. It crystallises from dilute alcohol in large prismatic crystals containing $2\frac{1}{2}H_2O$, losing $\frac{1}{2}H_2O$ on exposure to air. From ether rhombohedra containing $2H_2O$ are obtained, and from boiling water plates containing $1\frac{1}{2}H_2O$. From benzene anhydrous needles separate which melt with decomposition at 171·5° (corr.) $[\alpha]_D^{15°} = +236·5°$–3·0c in 97 p.c. alcohol, $c=1$–3. It is soluble in 6900 parts of water at 25°, 750 parts at 100°, 26 parts of alcohol at 20°, and in 22 parts of ether at 20°; slightly soluble in chloroform, benzene, amyl alcohol, and carbon disulphide.

Chemically, quinidine behaves similarly to quinine, yielding salts which, however, with the exception of the hydriodide, are more soluble than those of quinine. Its decomposition products are also the same as, or isomeric with, those of quinine. The disulphate on heating with acid gives quinicine. Treated with fuming sulphuric acid the alkaloid yields quinidine isosulphonic acid $C_{20}H_{23}O_2N_2 \cdot HSO_3$, identical with the product obtained from quinine under

similar treatment (Hesse, Annalen, 1892, 267, 141). By the action of permanganate in the cold a base quitenidine, isomeric with quitenine (*q.v.*) is obtained.

Quitenidine $C_{19}H_{22}O_4N_2$ forms thin plates from dilute alcohol, m.p. 246°, soluble in ammonia, from which solution it crystallises in large prisms on evaporation. It is readily soluble in boiling water, acids, and alkalis, less so in alcohol. Its H_2SO_4 solution is fluorescent and it gives the thalleioquin reaction, which on adding ferrocyanide turns violet-black. It yields a sulphate $B \cdot H_2SO_4,3H_2O$, colourless prisms; and a platinochloride $B \cdot H_2PtCl_6,3H_2O$, large orange-yellow crystals.

Apoquinidine $C_{19}H_{22}O_2N_2$, isomeric with apoquinine, is formed similarly by heating the base in a sealed tube to 140° with HCl (sp.gr. 1·125). It is a white amorphous powder, readily soluble in alcohol and ether, giving the thalleioquin reaction, but not showing fluorescence with H_2SO_4. It melts at 137° (uncorr.), and has $[\alpha]_D^{15°} = +153·3°$ in 97 p.c. alcohol, $c=2$. It yields a hydrochloride in needles easily soluble in water. Its acetyl derivative, unlike the base, fluoresces in H_2SO_4 solution.

Chloroquinidine $C_{20}H_{23}ON_2Cl$ is obtained similarly to its isomer, chloroquinine. It is readily soluble in alcohol, benzene or chloroform; m.p. 131°–132°. On treatment with alcoholic potash it gives the same product as chloroquinine, *i.e.* quinene.

Hydrochloroquinidine $C_{20}H_{25}ClO_2N_2$ is obtained similarly to its isomer, hydrochloroquinine It forms large crystals soluble in alcohol and in excess of ammonia. It gives the thalleioquin reaction. By longer heating methyl chloride is eliminated and hydrochlorapoquinidine results.

α-**Isoquinidine** $C_{20}H_{24}O_2N_2,2H_2O$ is formed together with hydrochloroquinidine by heating quinidine with HCl (sp gr. 1·189) at 85°. It forms fine rhombohedra soluble in ether.

Hydroiodoquinidine $C_{20}H_{25}IO_2N_2$ is obtained when quinidine is dissolved in 10 times its weight of HI (sp gr. 1·9) and left for 3 days in the dark. Its dihydriodide crystallises in large yellow tables, m.p. 230°, soluble in alcohol. Ammonia liberates the base, which is recrystallised from alcohol as colourless transparent prisms, m p. 205°–206°, slightly soluble in water. It gives the thalleioquin reaction and yields a crystalline sulphate, nitrate, hydrochloride, hydriodide, and platinochloride.

Quinidine Salts.—**Sulphate** $B_2 \cdot H_2SO_4,2H_2O$ crystallises as white needles or long hard prisms, soluble in 100 parts of water at 15°, or 7 parts at 100°, 20 of chloroform at 15°, insoluble in ether. The salt requires a temperature of 120° for dehydration, and reabsorbs $2H_2O$ on exposure to air. $[\alpha]_D^{17} = +211·5°$ in absolute alcohol, $c=1·94$ p.c. of hydrated salt. A chloroform solution gradually assumes a yellow colour with slight green fluorescence. On shaking this solution with water the aqueous portion acquires a beautiful green fluorescence.

Commercial quinidine sulphate is usually fairly pure; cinchonine is the most frequent impurity, cinchonidine and quinine being rarely found. To test for other alkaloids dissolve

0·5 gram in 20 c.c. of warm water, add 0·5 gram of KI, and stir vigorously for a few minutes. After half an hour filter off the insoluble hydriodide and add ammonia to the filtrate. If any decided precipitate occurs (none with the pure salt) shake with chloroform, evaporate the extract to dryness, and weigh. Test the residue for quinine, cinchonidine, and cinchonine. Should the two latter be present the precipitated hydriodide will tend to be resinous instead of sandy (De Vrij, Pharm. J. 1877, 8, 745).

Disulphate $B H_2SO_4,4H_2O$ occurs in long asbestos-like prisms, soluble in 7 parts of water at 15°, giving a beautiful blue fluorescence.

Other salts met with are: benzoate $B·C_7H_6O_2,H_2O$, soluble in alcohol; chromate $B·H_2CrO_4,6H_2O$, large yellow tables; hydrobromide $B·HBr$, soluble in 200 of water at 14°; hydrochloride $B·HCl,H_2O$, soluble in 75 parts of water at 15°, $[a]_D = +212°$ $-2·56c$ in alcohol; dihydrochloride $B·2HCl,H_2O$, very soluble in water; hydriodide $B·HI$, short prisms, soluble in 1250 of water at 15°, very slightly soluble in alcohol; dihydriodide $B·2HI,3H_2O$, large golden prisms, soluble in 90 of water at 15°; hyposulphite

$$B_2·H_2S_2O_3,2H_2O$$
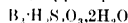
short prisms, soluble in 415 of water at 10°; oxalate $B_2·C_2H_2O_4,H_2O$, soluble in 151 of water at 15°, nitrate $B·HNO_3$, small prisms, soluble in 85 of water at 15°; phosphate $B·H_3PO_4$, short prisms, soluble in 31 of water at 10°; platinochloride $B_2·H_2PtCl_6,3H_2O$, orange needles; diplatinochloride $B H_2PtCl_6,H_2O$, yellow amorphous precipitate, insoluble in water; salicylate $B·C_7H_6O_3$, soluble in 1650 of water at 25°; succinate $B C_4H_6O_4,2H_2O$, fine prisms, soluble in 41 of water at 10°, very soluble in alcohol; sulphocyanide $B·HCNS$, colourless prisms, soluble in 1477 of water at 20°; disulphocyanide, $B 2HCNS,H_2O$, long yellow prisms, tannate, indefinite composition, soluble in about 1 in 2000 of water at 20°; tartrate

$$B_2·C_4H_6O_6,H_2O$$

silky prisms, soluble in 39 of water at 15°; bitartrate $B·C_4H_6O_6,3H_2O$, short prisms, soluble in 350 of water at 15°.

Hydroquinidine $C_{20}H_{26}O_2N_2$ usually occurs in commercial quinidine sulphate sometimes to the extent of 20 p.c. It may be separated by repeated recrystallisation from water, but it is preferably obtained by oxidising quinidine sulphate mother liquors with permanganate at 0° (v. Hydroquinine).

Quinidine may also be hydrogenated in the presence of palladium black yielding hydroquinidine. Forst and Bohringer's statement that this base is formed by the oxidation of quinidine is inaccurate, being due to their using quinidine containing hydroquinidine (Ber. 1881, 14, 1954; 1882, 15, 520, 854; Hesse, ibid. 1882, 15, 3010; Annalen, 1888, 243, 146). It forms efflorescent prismatic needles containing 2½H₂O, m.p. 167°, readily soluble in alcohol and chloroform, slightly soluble in ether. Its rotatory power is almost the same as that of quinidine. It gives the thalleioquin reaction and behaves generally like quinidine. Oxidation with chromic acid yields quininic acid.

Salts.—Its sulphate $B_2·H_2SO_4,2H_2O$ occurs as fine needles, soluble in 92·3 of water at 16°, or $B_2·H_2SO_4,8H_2O$, thick efflorescent prisms (Hesse). Its H_2SO_4 solution shows blue fluorescence. Other salts are: benzoate $B·C_7H_6O_2$, colourless plates; hydrobromide, fragile scales, slightly soluble in water; hydrochloride $B·HCl$, short needles or thick prismatic plates, readily soluble in water; hydriodide $B·HI$, large colourless needles, very slightly soluble in water; dihydriodide $B·2HI,3H_2O$, orange-yellow prisms, fairly soluble in water; platinochloride

$$B·H_2PtCl_6,2H_2O$$
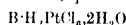
small orange-yellow needles; salicylate $B·C_7H_6O_3$, six-sided plates; tartrate $B_2·C_4H_6O_6,2H_2O$, brilliant prisms, readily soluble in water; bitartrate $B·C_4H_6O_6,3H_2O$, needles, slightly soluble in water.

Cinchonine, its Derivatives and Salts.—**Cinchonine** $(C_{19}H_{22}ON_2)$ occurs in all cinchona barks. It is readily prepared from quinine mother liquors, after removal of the cinchonidine as tartrate, by rendering alkaline and shaking with a limited quantity of washed ether. The cinchonine crystallises out from the ether in small hard prisms, and may be filtered off and recrystallised from dilute alcohol. The crystals melt at 264°, subliming with some decomposition at a higher temperature as monoclinic prisms. Ammonia precipitates the alkaloid from acid solutions in white flocks gradually becoming crystalline; but from hot solutions of ammonium salts cinchonine displaces ammonia. The freshly precipitated alkaloid is much more soluble in solvents generally than crystalline cinchonine. The crystals dissolve in 3670 of water at 20°, in 2500 of water at 100°, in 115 of absolute alcohol at 17°, in 356 of chloroform at 17°, in 371 of ether (sp gr 0·730) at 10°, in 40 of amyl alcohol at 17°, and in 18 parts of a mixture of alcohol and chloroform (4 : 1) at 17°. Readily soluble in acids, but the salts of cinchonine are liable to hydrolyse with water and deposit alkaloid Cinchonine is easily distinguished from the other alkaloids by giving neither fluorescent solutions nor an insoluble tartrate, and by being insoluble in ether. $[a]_D^{15°} = +226·5°$ in 97 p.c. alcohol, $c = 0·5$. Cinchonine does not give the thalleioquin reaction. On oxidation it yields the same products as quinine, except that the quinoline products lack the p-methoxy group.

Cinchotenine $C_{18}H_{20}O_3N_2$ is obtained on oxidising cinchonine with permanganate in acid solution (Skraup, Annalen, 1879, 197, 374). It is purified similarly to quitenine (q.v.). It forms efflorescent needles or plates containing $3H_2O$, m.p. 198°. $[a]_D^{15} = +135°$ in alcohol solution, $c = 2$ of hydrated base. A 2 p.c. solution in dilute H_2SO_4 gives $[a]_D^{15} = +175·5°$. It gives a platinochloride $B·H_2PtCl_6$, large orange prisms, and an aurichloride $B·H_2Au_2Cl_8$, yellow needles; both soluble in water and in alcohol.

Cinchotenicine $C_{18}H_{20}O_3N_2$, isomeric with cinchotenine, is formed from it by heating to 140° with H_2SO_4. A brown amorphous body soluble in water, giving amorphous platino- and auri-chlorides. $[a]_D^{15°} = +0·9°$.

Cinchoninic acid $C_9H_6 \cdot COOH \cdot N$ (4-carboxy-quinoline), obtained by oxidising cinchonine with chromic acid (v. Quininic acid). Forms caffeine-like needles containing $1H_2O$, or tables or prisms with $2H_2O$; m.p. $253°-254°$; subliming with decomposition (Caventou and Willm, Annalen, Supl 1870, 7, 247; Skraup, Annalen, 1880, 201, 294). It is only slightly soluble in water, more so in acids and alkalis, but its salts dissociate in water Heated with lime it yields quinoline. Permanganate oxidises it to α-carbocinchomeronic acid (Ramsay and Dobbie, Chem. Soc. Trans. 1884, 35, 189), nitric acid at $120°-140°$ yields cinchomeronic acid (Weidel, Annalen, 1874, 173, 76), and chromic acid gives kynurine (Skraup, Monatsh. 1888, 9, 783; 1896, 17, 366). On fusion with potassium hydroxide oxycinchoninic acid sublimes (Konigs and Kerner, Ber 1883, 16, 2152) Cinchoninic acid may also be prepared by oxidation of lepidine and 4-ethylquinoline

Cinchene $C_{19}H_{20}N_2$ is obtained by refluxing cinchonine chloride with alcoholic potash (v Quinene), as trimetric tables, m p $123° 125°$. It is a ditertiary base, soluble in ether, dextrorotatory, and yields crystalline salts. On hydrolysis with 25 p.c. phosphoric acid it yields lepidine and meroquinene. Chromic acid oxidises it to cinchoninic acid Treated with bromine in chloroform solution two isomeric dibromides (α and β) of cinchene are formed, both of which are converted into a new base, dehydrocinchene ($C_{19}H_{18}N_2$), with loss of 2HBr (Comstock and Konigs, Ber. 1886, 19, 2857). Chlorine reacts similarly to bromine with cinchene. On heating cinchene in a sealed tube with HBr (sp gr. 1·49) to 190° it loses a molecule of ammonia and adds a molecule of water to form apocinchene (v. Apoquinene)

Apocinchene $C_{19}H_{19}ON$, colourless needles, m.p. 209°, volatilising without decomposing, soluble in alcohol, acids, and alkalis (Comstock and Königs, Ber. 1881, 14, 1854; 1884, 17, 1989). Its salts give yellow solutions which readily hydrolyse, and its solutions in alkalis are precipitated by CO_2. It readily forms ethers, which with dilute HNO_3 oxidise to alkylapocinchenic acids. Chromic acid oxidises it to cinchoninic acid; and fusion with potassium hydroxide gives oxyapocinchene $C_{19}H_{19}O_2N$, a base isomeric with apoquinene.

Ethylapocinchenic acid   •

$$C_{17}H_{13} \cdot OC_2H_5 \cdot COOH \cdot N$$
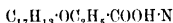
on refluxing with HBr (sp.gr. 1·49) gives rise to a lower homologue of apocinchene named homapocinchene $C_{17}H_{15}ON$. This body melts at $184°-185°$, is very soluble in ether, benzene, or hot alcohol, insoluble in water.

Dihydrocinchene $C_{19}H_{22}N_2$ was found by Königs in the mother liquors from apocinchene, and was derived from the hydrocinchonine present in the cinchonine from which the latter was prepared.

Cinchonine chloride $C_{19}H_{21}N_2Cl$, obtained similarly to quinine chloride (q.v.). It crystallises in prisms, melting at 72°, and is dextrorotatory. On reduction with iron and H_2SO_4 it gives desoxycinchonine $C_{19}H_{22}N_2$, m.p. $90°-92°$, dextrorotatory. With alcoholic potash cinchene is obtained (q.v.).

Cinchonine dichloride $C_{19}H_{22}ON_2Cl_2$ is made

by passing chlorine into a cooled HCl solution of cinchonine. It is very similar to dichlorocinchonine, and may be identical with it.

Dichlorocinchonine $C_{19}H_{20}OCl_4N_2$ is obtained by passing chlorine into a hot concentrated alcoholic solution of cinchonine hydrochloride. It crystallises as microscopic needles from alcohol, and gives crystalline salts with 2HCl, 2HBr, and H_2PtCl_6 (Laurent, Annal. Chim. Phys. (3) 24, 302).

Bromocinchonine $C_{19}H_{21}OBrN_2$ is formed by adding bromine to an alcoholic solution of cinchonine hydrochloride (Laurent, l.c.; Kopp, Arch. Pharm. (3), 9, 34). Its dihydrochloride crystallises in rhombic tables. Treated with alcoholic potash it exchanges Br for OH, and gives oxycinchonine $C_{19}H_{22}O_2N_2$.

Sesquibromocinchonine $C_{38}H_{41}O_2Br_3N_4$, obtained by the action of excess of bromine on an alcoholic solution of cinchonine. It crystallises in fine needles and forms salts with 4 molecules of monobasic acids. Treated with alcoholic potash it yields sesquioxycinchonine $C_{38}H_{44}O_4N_4$.

Dibromocinchonine $C_{19}H_{20}OBr_2N$, formed by adding excess of bromine to an aqueous solution of cinchonine hydrochloride (Comstock and Königs, Ber. 1884, 17, 1995). It gives colourless crystals containing $1H_2O$ from alcohol, insoluble in water. Alcoholic potash yields dioxycinchonine $C_{19}H_{22}O_3N_2$.

Cinchonine α- and β-dibromides

$$C_{19}H_{22}OBr_2N_2$$
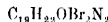
formed by adding bromine to a solution of cinchonine in chloroform and alcohol. The hydrobromide of the α-compound being less soluble than the β-compound crystallises out, the latter remaining in the mother liquor. The free α-base crystallises out from alcohol (90 p.c.) and chloroform (1 : 3) with $1H_2O$, the β-base being anhydrous. Both behave as true bases forming salts. Heated with alcoholic KOH they lose 2HBr, yielding a new base, dehydrocinchonine (Comstock and Konigs, Ber. 1886, 19, 2854; 1887, 20, 2510).

Hydrochlorocinchonine $C_{19}H_{23}ClON_2$, formed by allowing 10 parts of HCl saturated at $-17°$ to act on cinchonine at a low temperature for some weeks. The base crystallises from alcohol in white needles, m.p. $212°-213°$. Heated with alcoholic KOH an isomer of cinchonine, α-isocinchonine, is formed (Comstock and Königs, Ber. 1887, 20, 2519).

Hydrobromocinchonine $C_{19}H_{23}BrON_2$ is formed similarly to the last compound, but the reaction is more rapid and works equally well at higher temperatures. The base crystallises from alcohol in white scales. Heated with 85 p.c. alcohol it is converted into a mixture of apocinchonine, α-isocinchonine and δ-cinchonine. Heated with alcoholic KOH a mixture of apocinchonine α-isocinchonine and cinchonifine (?[*]hydrocinchonine) is formed.

Hydroiodocinchonine $C_{19}H_{23}ION_2$ is obtained by heating dry cinchonine with 5 parts of HI (sp.gr. 1·7) on the steam-bath. The free base crystallises from alcohol in silky needles melting at $158°-160°$ with decomposition. It readily combines with 2 molecules of monobasic acids to form crystalline salts.

**Dehydrocinchonine** $C_{19}H_{20}ON_2$, obtained from cinchonine dibromide (q.v.). It crystallises

from alcohol in needles melting at 202°–203°, subliming at a higher temperature; very soluble in alcohol, acetone, and chloroform, less so in ether or benzene. It behaves very similarly to cinchonine, giving salts and halogen derivatives containing H_2 less

Derivatives Isomeric with Cinchonine.— About 20 isomers of cinchonine have been described by various workers, but Skraup's investigations have shown that many of these bodies are identical, and several others are mixtures with cinchonine Hydrocinchonine has also been mistaken for an isomer of cinchonine (Monatsh 1897, 18, 411 ; 1899, 20, 571 ; 1901, 22, 1103 ; 1903, 24, 294 ; Langer, *ibid* 1901, 22, 151).

Cinchonicine (cinchotoxin) $C_{19}H_{22}ON_2$ occurs in commercial quinoidine, but may be prepared by heating the acid sulphate or tartrate of cinchonine or cinchonidine to 130°–140° (Pasteur, Compt. rend. 1853, 37, 110 ; Hesse, Annalen, 1875, 178, 213 ; D Howard, Chem. Soc Trans. 1872, 25, 102) It forms a viscid mass, yellow to red, melting at about 50°. Roques obtained it in long prismatic needles, m p 49°–50°, by evaporating an ethereal solution at 45°, in a current of hydrogen. $[a]_D^{15} = 47\cdot2°$ for 1 p c. solution in chloroform or absolute alcohol It is very soluble in alcohol or ether, slightly soluble in water. Its solutions absorb CO_2 from the air and expel ammonia from its salts. It gives the same oxidation products as cinchonine Like quinine, it gives a precipitate with hypo-chlorites, but does not give the thalleioquin reaction (distinction from quinine) Many of its salts are amorphous, but the following are crystalline : hydriodide $B\cdot HI$, prisms, slightly soluble in water ; oxalate $B_2\cdot C_2H_2O_4,7H_2O$, prisms, fairly soluble in water ; platinochloride $B\cdot H_2PtCl_6,H_2O$, bitartrate $B\,C_4H_6O_6,H_2O$.

Allocinchonine (pseudocinchonine)$C_{19}H_{22}ON_2$ is obtained by heating the hydriodide of hydroiodocinchonine $C_{19}H_{23}ION_2\cdot HI$ with 10 parts of water at 150°–160° It melts at 214°–216°, slightly soluble in alcohol or ether, and gives $[a]_D^{20} = +164\cdot8°$ for 3 p.c solution in absolute alcohol. Its sulphate $B_2\cdot H_2SO_4$ is less soluble in water than cinchonine sulphate. On oxidation it yields cinchoninic acid and allomeroquinene (Lippman and Fleissner, Monatsh 1893, 14, 371).

„**Tautocinchonine** $C_{19}H_{22}ON_2$ is obtained by the action of alcoholic KOH and silver nitrate on hydrobromocinchonine hydrobromide

$$C_{19}H_{23}BrON_2\cdot HBr$$
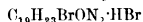
It is soluble in alcohol, slightly soluble in ether, m.p. 252·5°, and gives $[a]_D^{20} = |\ 209\ 4°$ for 3 p.c. solution in absolute alcohol (Löwenhaupt, Monatsh. 1898, 19, 461)

α-**Isocinchonine** (cinchoniline) $C_{19}H_{22}ON_2$ is obtained by heating cinchonine with sulphuric acid or HCl (sp gr. 1·125) ; or by heating hydrobromocinchonine or its salts with alcoholic KOH (Jungfleisch and Leger, Bull Soc. chim. 1888, 49, 747 ; Compt. rend. 1892, 113, 651 ; *ibid.* 1894, 118, 536 ; Hesse, Annalen, 1888, 243, 147 ; *ibid.* 1890, 260, 213 ; 1893, 276, 91 ; Comstock and Königs, Ber. 1887, 20, 2510 ; 1892, 25, 1539 ; Skraup, Monatsh. 1899, 20,

581 ; 1902, 22, 1097 ; Pum, *ibid.* 1892, 13, 676). It crystallises in silky needles from ether containing $3H_2O$; from petroleum ether in large prisms, volatile, m.p. 126·5°. $[a]_D^{15} = +51\cdot6°$ for 3 p.c. solution in absolute alcohol. It is readily soluble in ether, alcohol, or benzene, little soluble in water. It forms crystalline salts, all of which except the dihydriodide are very soluble in water. Heated with HCl (sp gr 1·125) at 140°–150° it is converted into apoisocinchonine (apocinchonigine), m p 216°, and with concentrated H_2SO_4 at 60°–80° it changes into β-isocinchonine. On oxidation it yields cinchoninic acid and α-isomeroquinene.

β-**Isocinchonine** (cinchonigine) $C_{19}H_{22}ON_2$, references under Isocinchonine. It crystallises from alcohol in colourless prisms, volatile, m.p $126°–127°$. $[a]_D^{18} = 59\cdot5°$ in absolute alcohol. Very soluble in alcohol, ether, or benzol. Its salts, including the dihydriodide, are very soluble in water. Heated with HCl (sp gr 1·125) it yields apoisocinchonine (apocinchinigine), m p. 216°. On oxidation it gives cinchoninic acid and β-isomeroquinene.

δ-**Cinchonine** $C_{19}H_{22}ON_2$ is formed at the same time as α-isocinchonine (q v.) when hydrobromocinchonine dihydrobromide is heated with alcohol or alcoholic KOH. Long prisms, m.p. 150°, very soluble in alcohol, benzene, or chloroform, slightly soluble in ether. $[a]_D^{17} = +125\cdot2°$ for 1 p c. solution in 97 p c. alcohol. Its salts are very soluble with the exception of the hydrochloride, hydrobromide, and oxalate (Jungfleisch and Leger, Compt. rend 1894, 118, 29)

ε-**Cinchonine** $C_{19}H_{22}ON_2$ was isolated by Löwenhaupt from tautocinchonine (q v.) It is a base melting at 150°–152°, giving crystalline salts $[a]_D^{20} = +67°$ for 1 p c. solution in alcohol.

Cinchonidine $C_{19}H_{22}ON_2$ was obtained in 5 p c. yield by Königs and Hussman from cinchonine by heating it for 15 hours with an amyl alcohol solution of KOH (Ber. 1896, 29, 2185)
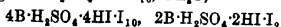
Hydro-derivatives of Cinchonine.—On reducing cinchonine with zinc and H_2SO_4, Schützenberger obtained a resinous body which he termed a hydrate of cinchonine, assigning to it the formula $C_{19}H_{22}ON_2,2H_2O$. This body is stable up to 120°, but at 140° it loses $\frac{3}{4}H_2O$, and at 150° retains $1H_2O$ (Annalen, 1858, 108, 348). Zorn reducing cinchonine with sodium amalgam in acetic acid obtained an oily mass containing two bases separated by ether. The one insoluble in ether he named hydrocinchonine, the dihydrodicinchonine of Skraup) $C_{19}H_{24}ON_2$, the other soluble in ether he called amorphous hydrocinchonine (the dihydrocinchonine of Skraup) $C_{19}H_{24}ON_2$. The first crystallises from alcohol in small colourless anhydrous plates or scales, m.p. 257°–258°. It yields a crystalline sulphate $B\cdot H_2SO_4,2H_2O$ (or anhydrous) in long needles. It is readily attacked by permanganate ; but on further treatment with sodium-amalgam is unattacked. The second dissolves in ether with a fine violet fluorescence, and is obtained as a yellowish amorphous mass on evaporation. It yields no crystalline salts or derivatives. It is a stronger base than cinchonine, dissolving in acids with elevation of

temperature, and is readily attacked by permanganate (Zorn, J. pr. Chem. 1873, 8, 279, 293; Skraup, Ber. 1878, 11, 312; Howard, Chem. Soc. Trans. 1873, 26, 1180). By the action of sodium and anhydrous amyl alcohol on cinchonine Norwall obtained an oily base $C_{19}H_{28}ON_2$, which he termed tetrahydrocinchonine (Monatsh. 1895, 16, 321).

None of the above is identical with the hydrocinchonine which occurs naturally in cinchona barks (Caventou and Wilm, Annalen, Supl. 1870, 7, 247; Forst and Bohringer, Ber. 1881, 14, 436; Hesse, Ber. 1895, 28, 1421).

Hydrocinchonine (Cinchotine) $C_{19}H_{24}ON_2$ is a constant associate of cinchonine, which may contain up to 10 p.c. It may be prepared similarly to hydroquinine (q.v.), by oxidation of the cinchonine with permanganate, or by saturating an alcoholic solution of cinchonine hydrochloride with HCl gas, when the dihydrochloride of cinchonine separates out, leaving the hydrocinchonine in solution (Hesse, Annalen, 1893, 276, 88). It forms slender anhydrous prisms or scales, m.p. 277°, subliming at higher temperature. Soluble in 136 parts of 90 p.c. alcohol, or 187 of ether at 20°; slightly soluble in boiling water. It is not attacked by cold permanganate, but chromic acid oxidises it to cinchoninic and cincholoiponic acids. With phosphorus pentachloride it yields hydrocinchonine chloride $C_{19}H_{23}ON_2Cl$, m.p. 85°–87°, converted by alcoholic KOH to dihydrocinchene $C_{19}H_{22}N$. Its chief salts are: benzoate $B \cdot C_7H_6O_2$, small needles, slightly soluble in water; hydrobromide $B \cdot HBr,2H_2O$; dihydrobromide $B \cdot 2HBr$, prismatic needles, very soluble in water, insoluble in alcohol; hydrochloride $B \cdot HCl,2H_2O$, needles, soluble in 47 of water; dihydrochloride $B \cdot 2HCl$, very soluble in water, slightly soluble in alcohol; hydriodide $B \cdot HI,H_2O$, colourless prisms, readily soluble in water and alcohol; nitrate $B \cdot HNO_3,H_2O$, transparent tables; oxalate $B \cdot C_2H_2O_4,H_2O$, fine needles, very slightly soluble in water; platinochloride $B \cdot H_2PtCl_6$, orange-yellow crystals; sulphate $B_2 \cdot H_2SO_4,12H_2O$, fine needles or prisms, efflorescent, soluble in 30·5 of water at 13°; sulphocyanide $B \cdot HCNS$, long needles, slightly soluble in water; tartrate $\cdot C_4H_6O_6,2H_2O,B_2$, needles soluble in 57 of water at 16°; bitartrate $B \cdot C_4H_6O_6,4H_2O$, needles, soluble in 78 of water at 16°.

Salts of Cinchonine.—**Cinchonine sulphate** $B_2 \cdot H_2SO_4,2H_2O$ forms short hard prisms or needles, melting at 198·5° when dehydrated, decomposing at 200°. It is soluble in 70 parts of water at 15°, in 13 parts at 100°, in 9 parts at 15°, in 60 of chloroform at 15° or in 22 at boiling-point, in 2300 of ether at 25°. As the sulphates of quinine and cinchonidine are insoluble in chloroform, this solvent forms a good test for the purity of cinchonine sulphate. A solution of this base in dilute H_2SO_4 does not fluoresce (although the commercial salt usually does so slightly owing to the presence of a little quinine or quinidine), nor does it give the thalleioquin reaction. With iodine it yields products analogous to herepathite, the principal being $8B \cdot 6H_2SO_4 \cdot 6HI \cdot I_{10},12H_4O$,

$$4B \cdot H_2SO_4 \cdot 4HI \cdot I_{10}, \quad 2B \cdot H_2SO_4 \cdot 2HI \cdot I_2$$

(Jörgensen).

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Cinchonine disulphate $B \cdot H_2SO_4,3$ or $4H_2O$, large colourless prisms, very soluble in water, and crystallising with difficulty.

Cinchonine hydrochloride $B \cdot HCl,2H_2O$ occurs as prismatic needles, melting at 130°. It is soluble in 24 parts of water at 10°, the solution dissociating slightly and depositing alkaloid. Soluble in 2 parts of 85 p.c. alcohol and 290 parts of ether at 15°.

Other salts are: benzoate $B \cdot C_7H_6O_2$, soluble in 166 of water at 15°; citrate $B_3 \cdot C_6H_8O_7,4H_2O$, soluble in 48 of water at 12°; acid citrate $B_2 \cdot C_6H_8O_7,4H_2O$, soluble in 55 of water at 15°; hydrobromide $B \cdot HBr,H_2O$, long needles, soluble in 33·5 of water at 15°, more soluble in alcohol; dihydrobromide $B \cdot 2HBr$, large rhombohedra, soluble in 1·4 of water at 15°, less soluble in alcohol; dihydrochloride $B \cdot 2HCl$, rhombic tables, very soluble in water, insoluble in alcohol; hydriodide $B \cdot HI,H_2O$, white crystals; dihydriodide $B \cdot 2HI,H_2O$, golden-yellow prisms, hydriodate $B \cdot HIO_3$, crystals, exploding at 120°; nitrate $B \cdot HNO_3,H_2O$, long monoclinic crystals, soluble in 26·4 of water at 12°; oxalate $B_2 \cdot C_2H_2O_4,2H_2O$, large prisms, soluble in 100 of water at 10°; platinochloride $B \cdot H_2PtCl_6$, pale yellow amorphous precipitate; succinate $B \cdot C_4H_6O_4,1$ or $1\frac{1}{2}H_2O$, long needles or thick prisms, readily soluble in water; sulphocarbolate $B \cdot C_6H_4 \cdot HSO_4 \cdot OH$, reddish-white needles; sulphocyanide $B \cdot HCNS$, prisms, soluble in 474 of water at 20°; salicylate $B \cdot C_7H_6O_3$, soluble in 590 of water at 25°; tartrate $B_2 \cdot C_4H_6O_6,2H_2O$, crystals, soluble in 33 of water at 16°; bitartrate (lævo-) $B \cdot C_4H_6O_6,H_2O$, soluble in 100 of water at 16°; bitartrate (dextro-), soluble in 101 of water at 16° (Pasteur).

Cinchonidine and its Derivatives and Salts.

Cinchonidine $C_{19}H_{22}ON_2$, a stereoisomer of cinchonine, occurs in most cinchona barks, especially in C. succirubra. It is prepared from quinine sulphate mother liquor by precipitation as neutral tartrate with Rochelle salt. This tartrate is washed with water and decomposed with ammonia, the rough base being dried carefully at a low temperature. On dissolving this in 2·1 c.c. of 50 p.c. H_2SO_4 and 11 c.c. of absolute alcohol for every gram of base, and allowing to cool, pure cinchonidine tetrasulphate crystallises out nearly quantitatively. This is filtered off, washed with absolute alcohol, dissolved in water, and precipitated as alkaloid with NaOH, being finally recrystallised from alcohol. It forms short anhydrous prisms or thin plates, soluble in 16 parts of 97 p.c. alcohol at 15°, in 188 parts of ether, or in 4800 parts of water at 25°; readily soluble in chloroform or amyl alcohol. It melts at 210·5°, and has $[\alpha]_D^{15} = -107 \cdot 48° + 0 \cdot 3c$ in 97 p.c. alcohol, $c=1$–5. Like cinchonine, its solutions do not fluoresce, nor give the thalleioquin reaction (distinction from quinine and quinidine). It differs from cinchonine in giving an insoluble tartrate, by its greater solubility in ether, and by being lævorotatory. For its estimation in cinchona barks, *see* under 'Quinine Sulphate.' It gives the same oxidation products as cinchonine with chromic or nitric acid; and cinchonicine, identical with that from cinchonine, is obtained by heating with glycerin to 200°,

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or with strong H_2SO_4 to 130°. The following are the most important derivatives of cinchonidine :—

Cinchotenidine $C_{18}H_{20}O_3N_2$, obtained similarly to quitenine by oxidation of cinchonidine with permanganate at 0°. It forms filiform or thick prismatic crystals containing $3H_2O$, slightly efflorescent. It melts at 256°, and has $[a]_D^{15} = -189°$ in alcohol. Its acid solutions do not fluoresce. Its salts are very soluble and difficult to crystallise It forms a sulphate $B_2 \cdot H_2SO_4.2\frac{1}{2}H_2O$, very soluble in water, and a platinochloride $B_2 H_2PtCl_6$, orange-yellow tables. Its solutions in alkalis are readily decomposed by CO_2 (Skraup, Annalen, 1880, 201, 300, Hesse, Ber. 1881, 14, 1892).

Cinchonidine chloride $C_{19}H_{21}N_2Cl$ is obtained by the action of phosphorus pentachloride on cinchonidine. It forms large crystals melting at 108°–109°, soluble in ether and possessing basic properties On heating with alcoholic KOH it yields cinchene (similarly to cinchonine chloride), which on treatment with HCl is converted to apocinchene

Dibromocinchonidine $C_{19}H_{20}ON_2Br_2$ is formed by adding 4 atoms of bromine to 1 molecule of cinchonidine suspended in CS_2. Its dihydrobromide crystallises in fine yellow needles readily soluble in alcohol (Skalweit, Annalen, 1874, 172, 103). On heating with alcoholic KOH it yields dioxycinchonidine.

Dioxycinchonidine $C_{19}H_{22}(OH)_2ON_2$ crystallises from alcohol in ramified crystals. It gives two sulphates, $B_2 \cdot H_2SO_4.2H_2O$ and $B \cdot H_2SO_4$, and a platinochloride $B H_2PtCl_6$

Hydrochlorocinchonidine $C_{19}H_{23}ClON_2$, formed by heating cinchonidine with HCl (sp.gr. 1·189) at 85° for two days. It is a base indistinguishable from hydrochloroapocinchonidine and is probably identical with it

Hydrochloroapocinchonidine $C_{19}H_{23}ClON_2$ is obtained together with apocinchonidine by heating cinchonidine in a sealed tube at 150° with fuming HCl for 6 hours. It crystallises in plates from alcohol, m p. 200°, $[a]_D^{15} = -142·2°$ in dilute HCl, slightly soluble in ether, chloroform, or alcohol It forms a dihydrochloride $B \cdot 2HCl$, very soluble in water, and a platinochloride $B \cdot H_2PtCl_6,2H_2O$ (Hesse, Annalen, 1880, 205, 327).

Hydroiodocinchonidine $C_{19}H_{23}ION_2$ is obtained by heating cinchonidine on the waterbath with 5 parts of HI (sp.gr. 1·7) for $2\frac{1}{2}$ hours It is a base very slightly soluble in hot alcohol, from which it falls on cooling as a crystalline precipitate, m.p. 166°. It gives a sulphate $B \cdot H_2SO_4$, soluble in 25 p c. alcohol. Heated with alcoholic KOH it yields an isomeride of cinchonidine, β-cinchonidine ; and with silver nitrate another isomeride, γ-cinchonidine (Neumann, Monatsh. 1892, 13, 651)

Derivatives Isomeric with Cinchonidine.—
Apocinchonidine $C_{19}H_{22}N_2$ is formed by the action of HCl on cinchonidine (r Hydrochloroapocinchonidine). Slightly soluble in strong alcohol, very slightly soluble in dilute alcohol, ether, or chloroform, almost insoluble in water. It forms small plates, m.p. 225°, with decomposition, and has $[a]_D^{15} = -129·2°$ for 0·8 p.c.

solution in 97 p.c. alcohol. It forms very soluble amorphous salts, whose acid solutions do not fluoresce, and is markedly different from cinchonidine in giving a soluble tartrate.

Isocinchonidine $C_{19}H_{22}ON_2$ is obtained as its sulphonate when cinchonidine is dissolved in fuming H_2SO_4. The base melts at 235°, and is very soluble in alcohol or chloroform, very slightly soluble in ether (Hesse, Annalen, 1888, 243, 149).

β-**Cinchonidine** $C_{19}H_{22}ON_2$ is obtained by heating hydroiodocinchonidine for 4 hours with alcoholic KOH, and is probably identical with Hesse's homocinchonidine It forms plates or prisms, m.p 207°, $[a]_D^{2°} = -181°$ for 1·25 p.c. solution in dilute HCl. On prolonged heating with HCl it is converted into apocinchonidine, from which it may be separated by means of its insoluble tartrate (Hesse, Annalen, 1880, 205, 327)

*Hydro-derivatives of Cinchonidine.—*On reduction with zinc and H_2SO_4, or sodium and alcohol, cinchonidine yields products very similar, chemically and physically, to those obtained from cinchonine Norwall describes a tetrahydrocinchonidine $C_{19}H_{26}ON_2$, obtained with sodium and pure amyl alcohol (Norwall, Ber 1896, 29, 801)

Hydrocinchonidine (cinchonidine) $C_{19}H_{24}ON_2$, usually accompanies cinchonidine in its commercial salts, and may be obtained from cinchonidine sulphate mother liquors by treatment with permanganate at 0° (r Hydroquinine). The base crystallises from dilute alcohol in hexagonal plates, and from strong alcohol in short anhydrous prisms, melting at 230° ; $[a]_D^{15} = -98 4°$ for 2 p c solution in 97 p.c. alcohol It is almost insoluble in ether, chloroform, or water, and less soluble in alcohol than cinchonidine Its salts crystallise readily and fluoresce in sulphuric acid solution (Hesse, Ber. 1881, 14, 1683 ; Forst and Bohringer, Ber. 1882, 15, 520).

*Salts of Cinchonidine.—***Cinchonidine sulphate** $B_2 H_2SO_4,3H_2O$ occurs as prismatic needles. From dilute aqueous solutions needles containing $6H_2O$ crystallise ; and from alcohol fine prisms with $2H_2O$. These salts are completely dehydrated at 100°, but absorb $2H_2O$ again on exposure to air. The anhydrous salt melts at 205° with decomposition. It is soluble in 100 parts of water, in 60 of alcohol, or 1000 of chloroform, at 15° ; soluble in 21 of water at 80° ; insoluble in ether or benzene. The commercial salt usually gives the thalleioquin reaction and fluoresces with dilute H_2SO_4 owing to the presence of quinine which may occur to even 60 p.c. Cinchonine and quinidine are also frequent impurities. A strong hot aqueous solution of the salt stirred with half its weight of Rochelle salt and allowed to cool and filtered, should not show more than a slight turbidity when the filtrate is treated with ammonia (Hesse, Zeitsch. anal. Chem. 1876, 15, 464).

Cinchonidine disulphate $B \cdot H_2SO_4,5H_2O$ occurs in long colourless efflorescent crystals, very soluble in water and alcohol (separation from quinine, *see* 'Assay').

Cinchonidine tetrasulphate $B \cdot 2H_2SO_4,2H_2O$, **for the preparation see under 'Quinine Sulphate.'**

Short colourless prisms, slowly soluble in cold water, almost insoluble in absolute alcohol.

Cinchonidine hydrochloride $B\cdot HCl, H_2O$ occurs as fine monoclinic prisms, soluble in 30 of water or 300 of ether at 12°; soluble in alcohol or chloroform. From alcohol fine needles containing $2H_2O$ are obtained.

Other salts are: benzoate $B\cdot C_7H_6O_2$, soluble in 333 of water at 10°; hydrobromide $B\cdot HBr, H_2O$ slightly soluble in water, more soluble in alcohol; dihydrochloride $B\cdot 2HCl, H_2O$, large prisms, very soluble in water and alcohol; hydriodide $B\cdot HI, H_2O$, colourless needles, slightly soluble in water; dihydriodide $B\cdot 2HI, H_2O$, lemon-yellow prisms; nitrate $B\cdot HNO_3, H_2O$, needles or large prisms, soluble in 71 of water at 10°; oxalate $B_2\cdot H_2C_2O_4, 6H_2O$, prisms, soluble in 250 of water at 10°; platinochloride $B_2\cdot H_2PtCl_6, 2H_2O$, small orange prisms, diplatinochloride $B\cdot H_2PtCl_6, H_2O$, orange-yellow crystalline powder, insoluble in water; salicylate $B\cdot C_7H_6O_3$, soluble in 77 of water at 18°; succinate $B_2\cdot C_4H_6O_4, 2H_2O$, small prisms, soluble in 583 of water at 10°; tartrate $B_2\cdot C_4H_6O_6, 2H_2O$, fine needles, soluble in 1265 of water at 10°, insoluble in Rochelle salt solution; acid tartrate $B\cdot 2C_4H_6O_6, 3H_2O$, long prisms.

Quinamine and its Derivatives and Salts.—

Quinamine $C_{19}H_{24}O_2N_2$ occurs in nearly all cinchona barks to a very small extent (Hesse, Annalen, 1873, 166, 266; Ber. 1877, 10, 2157). It accumulates in quinine sulphate mother liquors, from which it may be obtained by precipitating quinine and cinchonidine with Rochelle salt, precipitating the filtrate with ammonia and extracting the precipitate with ether. The ether is washed out with acetic acid, the acid solution neutralised, and while still warm treated with thiocyanate, until on cooling cinchonine can no longer be detected. The filtrate is precipitated with NaOH, and the resinous precipitate dissolved in a minimum of boiling 80 p.c. alcohol, from which quinamine crystallises on cooling. One gallon of quinine sulphate mother liquor will yield about 3 grams of quinamine. The base crystallises in delicate white anhydrous needles, melting at 172°, and has $[\alpha]_D^{15} = +94°$ for 1·5 p.c. solution in chloroform. It is nearly insoluble in cold water, soluble in 105 of 80 p.c. alcohol at 20°, and in 50 of ether (Oudemans, Annalen, 1879, 197, 150); also soluble in petroleum, ether, or benzene. Quinamine differs from the other cinchona bases in being monobasic, and therefore giving but one series of salts. It is coloured yellow by warm sulphuric acid, and orange by nitric acid.

The chief derivatives of quinamine are:—

Quinamicine $C_{19}H_{24}O_2N_2$, formed by heating quinamine for a few minutes at 100° with concentrated H_2SO_4. The product is treated with sodium bicarbonate, which precipitates the quinamicine in flocks, gradually becoming crystalline. It melts at 109°, has $[\alpha]_D^{15} = +3\cdot8°$ for 2 p.c. solution in alcohol, and is soluble in alcohol, chloroform, or ether (Hesse, Annalen, 1881, 207, 303). Its salts are amorphous.

Protoquinamicine $C_{17}H_{20}O_2N_2$ is formed by heating quinamine to 130° with concentrated H_2SO_4. It is an amorphous brown base.

Quinamidine $C_{19}H_{24}O_2N_2$ is formed when quinamine is heated with dilute mineral acids or with tartaric acid. Ammonia does not precipitate the base from its solution, but NaOH does so. It crystallises from alcohol in small white tufts of needles, not very soluble in ether or chloroform. It melts at 93°, and has $[\alpha]_D = +4\cdot5°$ for 2 p.c solution in alcohol. Heated with concentrated HCl it gives a yellow solution turning to brown, which on dilution turns rose, with a strong green fluorescence. Quinamidine yields a crystalline hydrochloride $B\cdot HCl, H_2O$, hydrobromide $B\cdot HBr, H_2O$: oxalate $B_2\cdot H_2C_2O_4, 4H_2O$; and a platinochloride $B_2\cdot H_2PtCl_6, 6H_2O$. Its hydrochloride gives a purple colour with $AuCl_3$ in aqueous solution.

Apoquinamine $C_{19}H_{22}ON_2$ is obtained by boiling quinamine or quinamicine with HCl (sp.gr. 1·125), or with 25 p.c. H_2SO_4 for 3 minutes (Hesse, Annalen, 1881, 207, 294). It crystallises in colourless scales, melting at 114°, soluble in alcohol, chloroform, or ether. Its alcoholic solution is optically inactive and neutral to litmus. It is a feeble base, but readily gives a crystalline hydrochloride $B\cdot HCl, \frac{1}{2}H_2O$ (levorotatory); nitrate $B\cdot HNO_3$; oxalate $B_2\cdot H_2C_2O_4, H_2O$; tartrate

$$B_2\cdot C_4H_6O_6, xH_2O;$$
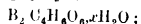
and platinochloride $B_2\cdot H_2PtCl_6, 2H_2O$.

*Salts of Quinamine.—*Quinamine gives a crystalline chlorate $B\cdot HClO_4$; perchlorate $B\cdot HClO_4$; hydrobromide $B\cdot HBr, H_2O$, thick prisms, very soluble in water or alcohol; hydrochloride $B\cdot HCl, H_2O$, colourless prisms, readily soluble in water; hydriodide $B\cdot HI$, small colourless prisms, soluble in 71 of water at 16°; nitrate $B\cdot HNO_3$, prisms, soluble in 16·5 of water at 15°, sulphate, hexagonal plates or short prisms, very soluble in water; and an amorphous yellow platinochloride

$$B_2\cdot H_2PtCl_6, 2H_2O$$
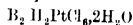
decomposing in the light.

Conquinamine and its Salts.

Conquinamine. $C_{19}H_{24}O_2N_2$, an isomeride of quinamine is found in the alcoholic mother liquor from which quinamine is crystallised, and is separated from it by fractional crystallisation of their nitrates, oxalates, or hydrobromides, the conquinamine salts being the more soluble (Oudemans, Annalen, 1881, 209, 38; Hesse, ibid. 62). It crystallises from alcohol in long prisms or pyramids, melting at 123°, and has $[\alpha]_D^{15} = +204\cdot4°$ for 1 p.c. solution in absolute alcohol. It is soluble in 7·4 parts of 91 p.c. alcohol at 19°; in 7·4 parts of ether at 15°; in 4·1 parts of benzene at 18°; almost insoluble in 50 p.c. alcohol or in water. It behaves very like quinamine and is monobasic, but its salts are generally the more soluble. Its oxalate, heated to 105°, melts and changes to quinamicine oxalate and then to apoquinamine oxalate. Heated with HCl (sp.gr. 1·125) it is converted into apoquinamine. Its acid solution with $AuCl_3$ gives a golden precipitate followed by a purple colouration.

*Salts.—*Acetate $B\cdot C_2H_4O_2$, dimetric crystals, soluble in 10·1 of water at 13·5°; chlorate $B\cdot HClO_3$, needles, soluble in 104 of water at

$16°$; perchlorate $B \cdot HClO_4$, long needles or short prisms, soluble in 396 of water at $16°$; formate $B \cdot CH_2O_2$, monoclinic crystals, soluble in $10 \cdot 8$ of water at $15°$; hydrochloride $B \cdot HCl$, large octahedra, moderately soluble in water; hydrobromide $B \cdot HBr$, monoclinic prisms, soluble in $25 \cdot 8$ of water at $16°$; hydriodide $B \cdot HI$, plates, soluble in 106 of water at $16°$; nitrate $B \cdot HNO_3$, rhombic crystals, soluble in 76 of water at $15°$; oxalate $B_2 \cdot C_2H_2O_4.3H_2O$, rhombic crystals, soluble in $82 \cdot 2$ of water at $17°$; quinate $B \cdot C_7H_{12}O_6.2H_2O$, prisms; platinochloride $B_2 \cdot H_2PtCl_6.2H_2O$, amorphous orange-yellow precipitate; sulphate $B_2 H_2SO_4$, long prisms, readily soluble in water or alcohol.

Amorphous Bases.

Diquinicine (diconquinine) $C_{40}H_{48}O_4N_4$ This amorphous base is the chief constituent of commercial quinoidine, and its constitution is very doubtful. Hesse found the molecular weight by the cryoscopic method to be about one-half of that represented by the above formula (Ber. 1877, 10, 2155) It is prepared by neutralising quinoidine with oxalic acid, thoroughly dehydrating, powdering the oxalate and extracting with cold chloroform. Quinicine oxalate remains undissolved, and on adding a little water to the chloroform solution and allowing to stand a short time, cinchonicine oxalate crystallises out, and is filtered off On evaporating the chloroform solution to dryness diquinicine remains as an amorphous red mass It is dextrorotatory, gives a fluorescent solution in dilute H_2SO_4, and gives the thalleioquin reaction. No crystalline salts have been obtained

Dicinchonicine (dicinchonine) $C_{38}H_{44}O_2N_4$. This base occurs in the bark of C rosulenta and C. succirubra, together with the principal cinchona bases It is prepared from the mother liquor, after precipitating the cinchonidine as tartrate, by rendering alkaline and extracting with ether. The ethereal solution is extracted with dilute acetic acid and the acid solution exactly neutralised with NaOH and fractionally precipitated with potassium sulphocyanide The dicinchonine thrown down, mainly in the middle fractions, is again put through ether and crystallised as hydrochloride (Hesse, Annalen, 1885, 227, 153). The free base is a yellow amorphous body with a strong alkaline reaction, m.p. $40°$, $[\alpha]_D^{15} = +91 \cdot 7°$ for a $1 \cdot 52$ p.c. solution in 97 p.c. alcohol. It is very soluble in ether, acetone, alcohol, chloroform, or benzene; insoluble in alkalis. The molecular weight determined by the cryoscopic method indicates half that of the above formula It gives a crystalline hydrochloride $B \cdot 2HCl$, easily soluble prisms; platinochloride $B \cdot 2H_2PtCl_6.4H_2O$, orange flakes; hydriodide, compact crystals, readily soluble in water, insoluble in NaCl or KI solution; and oxalate, easily soluble prisms; but its other salts are amorphous. On heating with HCl to $140°-160°$ it is converted into an isomeride, diapocinchonine, an amorphous base soluble in ether, alcohol, or chloroform, having $[\alpha]_D^{15} = +20°$ in alcoholic solution (Hesse, Annalen, 1880, 205, 333).

Paricine $C_{18}H_{18}ON_2$ was discovered by Winckler (Jahresber. 1845, 27, 338) in the barks

of Buena hexandra and C. lutea. Later, Hesse found it in C. succirubra of Darjeeling (Pharm. J. 1870, [3] 1, 344 ; Annalen, 1873, 166, 263). It is separated from the other cinchona bases by nitric acid, paricine nitrate being insoluble. The free base is obtained by suspending the nitrate in alcohol, decomposing with ammonia, and crystallising from petroleum ether. It is purified by dissolving in dilute HCl, decolourising with animal black and precipitating with ammonia. The pure paricine thus obtained is a yellow amorphous powder, soluble in water, alcohol, ether, and petroleum ether; m.p. $116°$. Its salts are amorphous.

Javanine was found by Hesse among the amorphous bases of C. Calisaya javanica. It separates from water in rhombic scales, very soluble in ether, and gives an intense yellow colour with dilute H_2SO_4. It yields a crystalline oxalate (Ber. 1878, 10, 2162).

REMIJIA BASES.

Cuprene and its Derivatives and Salts.— **Cupreine** $C_{19}H_{22}O_2N_2$ occurs in cuprea bark (Remijia pedunculata) together with the other cinchona alkaloids, except cinchonidine. Its molecular combination with quinine was at first mistaken for a new alkaloid, and called homoquinine (Howard and Hodgkin, Chem. Soc Trans. 1882, 41, 66 ; Paul and Cownley, Pharm. J. 1881, 12, 497). Three years later, Paul and Cownley isolated the new alkaloid cupreine from homoquinine (Pharm. J. 1884, 15, 221, 401 ; Hesse, Annalen, 1884, 225, 98 ; ibid. 226, 242 ; 1885, 230, 72). Cupreine completely crystallises out with the quinine when a sulphuric acid solution of the bases is neutralised. It is separated from the quinine by dissolving this rough sulphate in acid, precipitating the solution with excess of NaOH, and extracting the quinine with ether. The alkaline aqueous liquor on neutralising with H_2SO_4 throws out cupreine sulphate. The base crystallises from ether in concentric prisms containing $2H_2O$, or from alcohol as a crystalline powder containing $\frac{1}{2}H_2O$, dehydrating at $120°$. It is sparingly soluble in ether or chloroform, easily soluble in alcohol; m.p. $198°$, $[\alpha]_D^{16} = -175 \cdot 3°$ for $1 \cdot 5$ p.c. solution in 97 p.c. alcohol. Its solution in dilute H_2SO_4 does not fluoresce, but gives the thalleioquin reaction; and with ferric chloride a reddish-brown colour is obtained. Cupreine is the lower homologue of quinine having a hydroxyl group replacing the methoxy group of quinine in the para- position of the quinoline ring. This $-OH$ group has phenolic properties which enables cupreine to form salts with the alkalis, and strong compounds with the other cinchona bases. It is also dibasic, forming readily crystalline salts with acids. Heated with HCl (sp gr. $1 \cdot 125$) to $150°$ it is converted into an isomer, apoquinine, the same body being obtained from the other cinchona bases under similar treatment $(q\,v.)$. When sodium cupreïnate is treated in methyl alcohol solution with methyl chloride or methyl nitrate, quinine (methyl-cupreïne) is obtained (Grimaux and Arnaud, Compt. rend. 1891, 112, 374, 766 ; 114, 548, 612). By this reaction the following higher homologues of quinine were obtained by Grimaux and Arnaud :—

Quinethyline $C_{19}H_{20}N_2(OH)OC_2H_5$, a white powder, m.p. 160°, $[\alpha]_D = -169\cdot4°$; sulphate $B_2\cdot H_2SO_4,H_2O$, plates, soluble in 397 of water at 15°.

Quinpropyline $C_{19}H_{20}N_2(OH)OC_3H_7$, a white powder, m.p. 164°; sulphate $B_2\cdot H_2SO_4,1\frac{1}{2}H_2O$, needles, soluble in 454 of water at 13°.

Quinisopropyline $C_{19}H_{20}N_2(OH)OC_3H_7$, a white powder, m.p. 154°; sulphate $B_2\cdot H_2SO_4,H_2O$, needles, soluble in 367 of water at 10°.

Quinisoamyline $C_{19}H_{20}N_2(OH)OC_5H_{11}$, amorphous, m.p. 167°; sulphate $B_2\cdot H_2SO_4$, needles, soluble in 4170 of water at 11·5°.

These ethers all give fluorescent solutions in dilute H_2SO_4, whereas cupreine does not. They are strongly febrifugal, but more toxic than quinine.

Homoquinine. The molecular compound of quinine and cupreine named homoquinine

$$C_{20}H_{24}O_2N_2\cdot C_{19}H_{22}O_2N_2,1, 2, \text{ or } 4H_2O$$
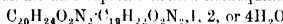
may be obtained by dissolving equi-molecular proportion of the two alkaloids in alcohol and evaporating to dryness, or by mixing 1 molecule of quinine hydrochloride with 1 molecule of sodium cupreinate (Hesse, *l.c.*). It behaves like a simple alkaloid, alkalis alone breaking it up, and forms well-defined salts. It melts at 177°, is lævorotatory, and dissolves with difficulty in ether, but readily in alcohol.

For Hydrocupreine, *see* 'Hydroquinine.'

Salts of Cupreine.—Acetate $B\cdot C_2H_4O_2,2H_2O$, fine needles, soluble in 85 of water at 17°; hydrobromide $B\cdot HBr,H_2O$, needles, soluble in 122 of water at 16°; dihydrobromide $B\cdot 2HBr$, soluble in 12·5 of water at 16°; hydrochloride $B\cdot HCl,H_2O$, small needles, soluble in 53·5 of water at 16°; dihydrochloride $B\cdot 2HCl$, short prisms, readily soluble in cold water; hydriodide $B\cdot HI$, soluble in 106·6 of water at 16°; dihydriodide $B\cdot 2HI,H_2O$, orange crystals, soluble in 15 of water at 16°; nitrate $B\cdot HNO_3,2H_2O$, needles, soluble in 86 of water at 16°; dinitrate $B\cdot 2HNO_3,H_2O$, yellow transparent crystals, soluble in 12·2 of water at 17°; oxalate $B\cdot C_2H_2O_4,2H_2O$, colourless crystals, soluble in 407 of water at 18°; platinochloride
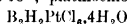
$$B_2H_2PtCl_6,4H_2O$$

yellow amorphous precipitate; diplatinochloride $B\cdot H_2PtCl_6,H_2O$, orange needles; sulphate $B_2H_2SO_4,6H_2O$ (Hesse), anhydrous (Howard and Chick, J. Soc. Chem. Ind. 1909, 28, 53), needles, soluble in 813 of water at 17°; disulphate $B\cdot H_2SO_4,H_2O$, thick prisms, soluble in 70·4 of water at 16°; tetrasulphate

$$B\cdot 2H_2SO_4,3H_2O$$

short silky needles, very soluble in water, less soluble in alcohol; tartrate $B_2\cdot C_4H_6O_6,H_2O$, white needles, soluble in 517 of water at 16°.

Cinchonamine and its Salts.—**Cinchonamine** $C_{19}H_{24}ON_2$ occurs in the bark of Remijia Purdieana, together with cinchonine, concusconine, chairamine, chairamidine, conchairamine, and conchairamidine. It is obtained by extracting the powdered bark with hot dilute H_2SO_4, the acid extract is precipitated by ammonia, and the precipitated bases filtered and dried. This dried mass is then extracted with boiling alcohol, the alcohol extract concentrated, cooled, and treated with HNO_3 (sp.gr. 1·200) until decidedly acid. Cinchonamine nitrate is

precipitated and is purified by recrystallisation from boiling water (Arnaud, Compt. rend. 1881, 93, 593; 1885, 97, 174; Hesse, Annalen, 1884, 225, 218).

The base crystallises in needles or orthorhombic prisms, melting at 185°, and subliming, $[\alpha]_D^{15} = +121\cdot1°$ for 2 p.c. solution in 97 p.c. alcohol. It dissolves in alcohol or chloroform, and in 100 of ether at 17°; slightly soluble in benzene, petroleum ether, CS_2, or water. It is a strong base, giving well-defined salts, and differs from its isomerides, hydrocinchonine and hydrocinchonidine, in being readily attacked by permanganate at 0° in H_2SO_4 solution. It differs from the cinchona bases in the great solubility of its sulphate and the insolubility of its nitrate. Arnaud proposed the use of this alkaloid for the estimation of nitrates, but the method is limited in its application (Ann. Chim. Phys. 1890, 19, 93; Howard and Chick, J. Soc. Chem. Ind. 1909, 28, 53). Treated with excess of nitric acid (sp.gr. 1·06) a yellow amorphous explosive body, dinitrocinchonamine

$$C_{19}H_{22}(NO_2)_2ON_2$$
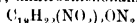
is formed, soluble in alcohol, chloroform, or ether, and melting at 118°. This base is insoluble in strong HCl, but soluble in the dilute acid; and on heating with strong HCl does not give methyl chloride. It is strongly febrifugal, but also very toxic.

Salts.—Citrate $B_2\cdot C_6H_8O_7$, prisms, soluble in 51 of water at 15°; hydrobromide $B\cdot HBr$, long needles, soluble in 600 of water at 15°; hydrochloride $B\cdot HCl$, soft laminæ, or $B\cdot HCl,H_2O$, transparent cubes, both soluble in 200 of water at 27° (Howard and Perry, J. Soc. Chem. Ind. 1905, 24, 1281); hydriodide $B\cdot HI$, long prisms or plates, soluble in 950 of water at 15°; hyposulphite $B\cdot H_2S_2O_3$, prisms, slightly soluble in water; malate $B_2\cdot C_4H_4O_5,H_2O$, flaky crystals, soluble in 100 of water at 15°; nitrate $B\cdot HNO_3$, short prisms, soluble in 500 of water at 15°; platinochloride $B_2\cdot H_2PtCl_6$, semi-crystalline yellow precipitate, insoluble in water; picrate $B\cdot C_6H_2(NO_2)_3\cdot OH,\frac{1}{2}H_2O$, yellow flocks, insoluble in water; sulphate $B_2\cdot H_2SO_4$, transparent prisms, very soluble in water, less soluble in alcohol; disulphate $B\cdot H_2SO_4$, octahedra or prisms,· very soluble in water; sulphocyanide $B\cdot HCNS$, laminæ or short prisms, insoluble in water; tartrate $B_2\cdot C_4H_6O_6$, crystalline powder or thick prisms, soluble in 87 of water at 15°.

Concusconine $C_{23}H_{26}O_4N_2$. To produce this base Hesse extracted Remijia Purdieana with alcohol, evaporated the extract to dryness, added a large excess of NaOH, and extracted with ether. On shaking the ethereal extract with excess of dilute H_2SO_4 the concusconine is precipitated as sulphate together with the chairamine isomerides; the cinchonine and cinchonamine remaining in the acid solution. The rough sulphate is boiled with Na_2CO_3 solution, and the freed bases washed, dried, weighed, dissolved in boiling alcohol, and 1 part of H_2SO_4 added for every 8 parts of alkaloid. Concusconine sulphate separates out completely on cooling (Annalen. 1884, 225, 234). The base forms colourless monoclinic prisms containing $1H_2O$; m.p., after drying, 206°-208° with decomposition; $[\alpha]_D^{15} = +40\cdot8°$ for 2 p.c. solution

in 97 p.c. alcohol. It is slightly soluble in strong alcohol, less so in dilute, very soluble in chloroform, ether, or benzene. A solution in acetic acid or HCl gives a dark-green colour with concentrated HNO_3. This reaction is also given with the chairamine isomerides. Concentrated H_2SO_4 gives a bluish-green solution, turning olive-green on warming. It is a weak base, its alcoholic solution being neutral to litmus. Its salts are mostly gelatinous, but it gives a crystalline sulphate $B_2 \cdot H_2SO_4$ in small white prisms almost insoluble in water or alcohol ; an oxalate $B_2 \cdot C_2H_2O_4$; and a platinochloride $B \cdot H_2PtCl_6$ Concuscomine is isomeric with brucine It contains two methoxy groups.

Chairamine $C_{22}H_{26}O_4N_2$. On adding a little concentrated HCl to the alcoholic mother liquor of the concusconine sulphate (above), chairamine hydrochloride crystallises out in small needles. The base crystallises from dilute alcohol in slender white needles or from strong alcohol in thick prisms containing H_2O, which melt at 140°, and, after drying, at 233° ; $[a]_D$= about +100 in 97 p c. alcohol It is readily soluble in chloroform or ether, and in 540 of 97 p c alcohol at 11°. Its acetic acid solution gives a dark-green colour with concentrated HNO_3. In concentrated H_2SO_4 the base gives a colourless solution, slowly turning dark green. It gives a hydrochloride $B \cdot HCl, H_2O$, needles, soluble in water, slightly soluble in alcohol a platinochloride $B \cdot H_2PtCl_6, 2H_2O$; and a sulphate $B_2 \cdot H_2SO_4, 8H_2O$.

Conchairamine $C_{22}H_{26}O_4N_2$. On adding a little solution of potassium sulphocyanide to the chairamine hydrochloride mother liquor (above), conchairamine sulphocyanide is obtained The base is liberated with NaOH and recrystallised from alcohol. Thick colourless prisms $B \cdot H_2O \cdot C_2H_5OH$ are obtained, melting at 82°-86°, and losing their water and alcohol of crystallisation at 120°, being at the same time converted into an amorphous form. An acetic acid solution of the base precipitated with ammonia yields white crystalline flocks containing H_2O, melting and dehydrating at 110°. The anhydrous base melts at 120°, and has $[a]_D^{15} = +68 \cdot 4°$ for 2 p c solution in 97 p.c. alcohol. It is soluble in chloroform or ether and in boiling alcohol In concentrated H_2SO_4 the base gives a brown solution turning dark green. It gives a dark-green colour in acetic acid solution with concentrated HNO_3 A solution of the base in alcohol is neutral to litmus. Its salts are readily crystalline, the chief being : hydrochloride $B \cdot HCl$; hydriodide $B \cdot HI, H_2O$; platinochloride $B \cdot H_2PtCl_6, 5H_2O$; sulphocyanide $B \cdot HCNS, H_2O$; sulphate

$$B_2 \cdot H_2SO_4, 9H_2O$$
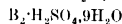
Chairamidine $C_{22}H_{26}O_4N_2$. When more potassium sulphocyanide is added to the filtrate from the conchairamine sulphocyanide until the dark colour of the solution becomes light brown a pitch-like mass separates. The mother liquor is now treated with excess of ammonia and shaken out with benzene ; the benzene is extracted with acetic acid and the acid solution treated with a saturated solution of ammonium sulphate, when a mixture of chairamidine and conchairamidine sulphate is precipitated. The mixed

sulphates are dissolved in boiling water and cooled, a gelatinous mass precipitating. part of which becomes crystalline after standing some days. On now warming to 40°, the gelatinous part redissolves, leaving the crystals of conchairamidine sulphate. On re-cooling chairamidine sulphate falls again as a jelly, which is drained off, re-dissolved in water, and the base precipitated with ammonia.

Chairamidine is a white amorphous powder containing H_2O, melting, when dry, at 126°-128° with decomposition, and has $[a]_D^{15} = +7 \cdot 3°$ for 3 p c solution in 97 p c. alcohol It is insoluble in water, readily soluble in alcohol, ether, chloroform, or benzene It is a feeble base, its alcoholic solution being neutral to litmus. It gives a yellow solution in concentrated H_2SO_4, slowly turning green. Animal black completely removes it from its solution in acetic acid Its salts, which are amorphous, have been little studied

Conchairamidine $C_{22}H_{26}O_4N_2$. This base is obtained as crystalline sulphate in the preparation of chairamidine (above). The free base is crystalline, contains H_2O, melts at 114°-115° after drying, and has $[a]_D^{15} - 60°$ for 3 p.c. solution of the anhydrous base in 97 p c alcohol. It is very soluble in alcohol, ether, chloroform, benzene, or acetone It is a feeble base and neutral to litmus It gives a dark green colour in concentrated H_2SO_4. It gives crystalline salts, the chief being hydrochloride $B \cdot HCl, 3H_2O$; platinochloride $B \cdot H_2PtCl_6, 5H_2O$; sulphate $B_2 \cdot H_2SO_4, 14H_2O$.

CUSCO BASES.

Aricine $C_{23}H_{26}O_4N_2$. This alkaloid was discovered in Cusco bark by Pelletier and Corriol (J. Pharm Chim 1829, 15, 575), and is identical with Manzini's cinchovatine Hesse obtained this base by extracting the powdered bark with alcohol, treating the alcoholic extract with excess of NaOH, and extracting with ether. The ethereal solution was shaken out with acetic acid, and the acid solution partially neutralised with ammonia, when aricine acetate separates out The filtrate mixed with a strong solution of ammonium sulphate, yielded cusconine sulphate (Annalen, 1878, 185, 296). Moissan and Landrin, after powdering the bark, treating it with lime and 40 p.c. NaOH and re-drying, extract the alkaloids with ether. On washing out the ethereal solution with dilute H_2SO_4 aricine sulphate falls out, is decomposed with ammonia, and the free base crystallised from alcohol (J Pharm. Chim. 1890, [5] 21, 337).

Aricine forms large colourless prisms, insoluble in water, soluble in 100 of 90 p.c. alcohol, or in 33 of ether, at 15° ; very soluble in chloroform. It melts at 188° and has $[a]_D^{15} = -58 \cdot 2°$ for 2 p.c. solution in 97 p.c. alcohol. In acid solution it is dextrorotatory, $[a]_D = +14 \cdot 5°$. It gives a yellow-green colour in strong H_2SO_4, turning a fine deep blue on addition of ammonium molybdate, which on warming turns olive-green, reverting to blue on cooling. This reaction is characteristic for aricine and cusconine. Nitric acid colours aricine deep green, and dissolves

it to a greenish-yellow solution. Aricine is not bitter in flavour, but slightly astringent. It is a feeble base, its salts partly dissociating in water.

The chief salts are : acetate

$$B \cdot C_2H_2O_4,3H_2O$$
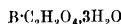
small white granular crystals, almost insoluble in cold water, slightly soluble in hot ; citrate $B \cdot C_6H_7O_6$, colourless needles, slightly soluble in water ; hydrochloride $B \cdot HCl,2H_2O$, colourless prisms, slightly soluble in cold water ; hydriodide $B \cdot HI$, colourless prisms, almost insoluble in water ; oxalate, granular white crystalline powder ; binoxalate $B C_2H_2O_4,2H_2O$, prisms, rapidly changing to rhombohedra, soluble in 2025 of water at 18°, platinochloride $B_2 \cdot H_2PtCl_6,5H_2O$, orange-yellow precipitate, sparingly soluble in water ; salicylate

$$B C_7H_6O_3,2H_2O$$
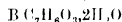
pale yellow pulverulent precipitate, sparingly soluble in water, easily soluble in alcohol ; sulphate $B_2 H_2SO_4$, fine needles, fairly soluble in cold water, disulphate $B H_2SO_4$, small crystalline groups, very slightly soluble in cold water ; sulphocyanide $B \cdot HCNS$, small colourless prisms, very slightly soluble in water.

Cusconine $C_{21}H_{26}O_4H_2$. The rough cusconine sulphate, obtained from the aricine acetate mother liquid (above), on precipitation with ammonia as the base and crystallising from ether, is obtained as white laminæ. From alcohol or acetone larger crystals may be obtained. The crystallised base contains $2H_2O$, which it loses at 80°, the anhydrous base melting at 110°. It has $[a]_D^{15} - 54.3°$ for a 2 p c solution in 97 p c alcohol. The base dissolves in 35 parts of ether at 15°, more easily in alcohol or acetone, is very soluble in chloroform, but is insoluble in water. It gives the same colour reactions with H_2SO_4 and ammonium molybdate as aricine. It is a feeble base, its salts having an acid reaction Most of the salts are gelatinous or amorphous Hesse (Annalen, 1878, 185, 296) prepared the following salts : aurichloride, dirty yellow amorphous precipitate readily decomposing ; hydrobromide, white amorphous precipitate, soluble in water ; hydrochloride, uncrystallisable, but forms with mercuric chloride a pulverulent precipitate $B \cdot HCl \cdot HgCl_2,2H_2O$; hydriodide, pale yellow amorphous precipitate, freely soluble in water ; platinochloride $B_2,H_2PtCl_6,5H_2O$, amorphous flocculent dark yellow precipitate ; sulphate $B_2H_2SO_4$, laminæ from alcohol ; disulphate, gelatinous and uncrystallisable ; thiocyanate $B \cdot HCNS,2H_2O$, pale yellow amorphous powder.

Cusconidine, an amorphous base precipitated from cusconine mother liquors with alkalis ; it falls as pale yellow flakes which, after washing, mass together, and on drying form an amorphous mass (Hesse, Annalen, 1880, 200, 303).

Cuscamine. From an acetic acid solution of the total alkaloids of Cusco bark nitric acid precipitates insoluble cuscamine and cuscamidine nitrates. On conversion of the nitrates to oxalates, and washing with water, cuscamidine oxalate dissolves, leaving cuscamine oxalate. The free base is obtained by treating with NaOH, and crystallising from ether and alcohol. Cuscamine forms colourless prisms, m.p. 218°

(uncorr.), with decomposition, very soluble in ether, moderately soluble in alcohol. It gives a yellow colour with concentrated H_2SO_4, turning brown on warming ; on adding molybdic acid a bluish-green colour is obtained, turning brown on heating, and violet-brown on re-cooling. With nitric acid a yellow colouration is obtained. It readily yields crystalline salts (Annalen, 1880, 200, 304).

Cuscamidine is obtained by concentration of its oxalate solution obtained as above. It closely resembles cuscamine in chemical and physical properties, but its salts are more soluble

ASPIDOSPERMA BASES.

Paytine $C_{21}H_{24}ON_2$ is extracted from the white bark of Payta (Peru) by means of alcohol. The alcoholic extract is dried, mixed with NaOH, shaken with ether, the ethereal solution extracted with dilute H_2SO_4, the acid liquor treated with animal charcoal and neutralised with ammonia   On adding KI solution until no more precipitation occurs, paytine hydriodide falls as a white precipitate, becoming dense, yellow, and crystalline. The free base crystallises in fine prisms containing H_2O, and is soluble in alcohol, ether, benzol, ligroin, and chloroform, slightly soluble in water ; m p. 156°, $[a]_j = -49.5°$ in 0.45 p c. alcoholic solution. An alcoholic solution is alkaline to litmus The base has a bitter flavour, but is not toxic. It gives curious characteristic colour reactions. With concentrated HNO_3 it gives a colourless solution passing through garnet-red to yellow. Its hydrochloride yields with platinum chloride a dark yellow precipitate, dissolving in HCl to a reddish-brown solution, turning blue and giving a blue precipitate. Bleaching powder produces in acid solution a dark red colour, turning blue and then pale yellow with precipitation. Gold chloride gives a purple colour and precipitate ; mercuric chloride a yellow amorphous precipitate. It gives several crystalline salts, the chief being the hydrochloride $B \cdot HCl$, prisms, soluble in 16.6 of water at 15°. Heated with soda-lime it yields a non-nitrogenous body, *paytone* (Hesse, Annalen, 1870, 154, 287 ; 1873, 166, 259 ; 1882, 211, 280 ; Ber. 1881, 13, 2308 ; Wulfsberg, Pharm. Zeit. 1880, 546 ; Arata, Gazz. chim. ital. 1881, 11, 246).

Paytamine $C_{21}H_{24}ON_2$ is an amorphous alkaloid precipitated from the iodide mother liquor of paytine hydriodide (see above) by alkalis. It is readily soluble in ether, gives a purple colour with gold chloride, but differs from paytine in yielding a soluble hydriodide, and by not giving paytone on heating with soda-lime.   B. F. H. & O. C.

CINEOL v. CAMPHORS, SANTONICA. For method of estimating cineol in volatile oils, see Dodge, Analyst, 1912, 461. For its solubility in water, see Earle, J. Soc. Chem. Ind. 1918, 274 T.

CINNABAR. Native mercury sulphide (HgS), and the only ore of this metal. Its crystals are rhombohedral, with perfect cleavages parallel to the faces of the hexagonal prism ; they are of interest crystallographically in presenting the same type of trapezohedral symmetry as quartz,

and, like this, they rotate the plane of plane-polarised light. They are bright-red in colour, often transparent, and have a brilliant adamantine to sub-metallic lustre; the scarlet streak is characteristic. Sp.gr. 8·1; hardness, 2–2½. The refractive indices are high : for the ordinary ray 2·854, and for the extraordinary ray 3·201 for red light. The massive ore, which may be compact or earthy in texture, is of the same colour; but sometimes it is liver-brown or black, owing to the admixture of clay or organic matter, as in the varieties called respectively *hepatic cinnabar* and *coral-ore* (German, *Korallenerz*). Cinnabar is very sporadic in its distribution, and no mineral containing mercury has yet been found in the British Isles It is mined at Almaden in Spain ; Monte Amiata in Tuscany ; Idria in Carniola, New Almaden in California ; in the provinces of Kwei-chou and Hunan, in central China ; and in Mexico and Peru.

Cinnabar and two other crystalline modifications of mercuric sulphide have been obtained artificially by E T Allen and J. L. Crenshaw (1912). Cinnabar is the stable form at all temperatures up to its sublimation point, about 580°.   L. J. S.

CINNABAR, AUSTRIAN, *v* CHROMIUM.

CINNAMALDEHYDE, *Cinnamic aldehyde* $C_6H_5\cdot CH:CH\cdot CHO$, is contained, together with a hydrocarbon, in oil of cinnamon and oil of cassia. It may be extracted from oil of cinnamon by shaking the oil with a concentrated solution of sodium bisulphite, filtering off the crystalline bisulphite compound, washing the latter with alcohol and distilling it with dilute sulphuric acid, when the cinnamaldehyde passes over with the steam. The cinnamaldehyde is extracted from the aqueous distillate with ether, and, after expelling the ether, is purified by distillation under a pressure of from 40 to 50 mm (Peine, Ber. 1884, 2109) It may be extracted from cassia oil by adding to it the barium salt of sulphanilic acid, filtering off the crystalline compound thus formed and steam distilling, whereby the compound is resolved into its components and cinnamaldehyde distils over (Ch. Fab. von Heyden Akt.-Gesel. D. R. P. 124229 ; Chem. Zentr. 1901, ii. 903). It is obtained by allowing a mixture of 10 parts of benzaldehyde, 15 of ordinary aldehyde, 900 of water, and 10 of a 10 p c solution of caustic soda to stand at a temperature of about 30° for from 8 to 10 days, shaking from time to time :

$$C_6H_5\cdot CHO + CH_3\cdot CHO = C_6H_5\cdot CH\cdot CH\cdot CHO + H_2O$$
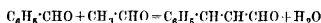
The solution is extracted with ether and the ethereal extract treated as in the foregoing method (Krszysica, Ber. 1884, 2117). It is best prepared by the condensation of benzaldehyde and ordinary aldehyde at a low temperature by means of a concentrated alkali solution. The alcoholic solution of the aldehydes, cooled to −10°, is agitated with a 25–30 p.c. solution of caustic soda, previously cooled to the same temperature. Under these conditions the formation of resins is avoided (Boehringer and Söhne, Eng. Pat. 10003 ; J. Soc. Chem. Ind. 1897, 463). Also formed when a mixture of calcium cinnamate and calcium formate is distilled (Piria, **Annalen, 100,** 105).

It is a colourless oil with a pleasant aromatic smell of cinnamon. It decomposes when distilled under ordinary pressures, especially with access of air, but may be distilled without decomposition in a current of steam or under reduced pressure. It boils at 120°–130° under a pressure of 20 mm. (Peine, Ber. 1884, 2110) ; at 209·5° under 250 mm (Perkin, Chem. Soc. Trans. 1896, 1247) and solidifies at −7·5° (Pictet, Compt. rend. 119, 955) ; sp.gr. 1·0497 20°/4° (Brühl, Annalen, 235, 18).

By oxidation it yields first cinnamic acid and afterwards benzaldehyde and benzoic acid. Direct reduction does not lead to cinnamyl alcohol as the aldehyde polymerises. Reduction with the zinc-copper couple gives rise to hydrocinnamoin $C_6H_5(OH)_2(CH : CHPh)_2$ (Thiele, Ber. 1899, 1296). It gives the usual reactions of the aldehydes The diacetyl derivative of the aldehyde, obtained by the action of acetic anhydride, can, however, be easily reduced by iron in acetic acid solution, and by subsequent saponification the alcohol is obtained (Barbier and Leser, Bull Soc chim 1905, 858).

Estimation — To estimate cinnamic aldehyde in oil of cinnamon or oil of cassia, 10 c c. of the oil are heated on the water-bath, and a solution of sodium bisulphite added in small quantities, time being allowed for the solid to liquefy between each addition The precipitate is filtered off and weighed (Schimmel, Chem Zentr. 1892, i. 92). Hanus (J Soc Chem Ind 1903, 1154) estimates cinnamaldehyde by means of its semioxamazone. *See also* Burgess, Analyst, 29, 78.

It may be estimated colorimetrically by the reaction it develops on treatment with sulphuric acid and isobutyl alcohol (Jellenberg).

CINNAMEÏN *v* *Balsam of Peru*, art. BALSAMS.

CINNAMIC ACID $C_6H_5\cdot CH:CH\cdot COOH$. (*Acide cinnamique*, Fr. ; *Zimmtsäure*, Ger) *β-Phenylacrylic acid* The separation of a solid acid from oil of cinnamon on keeping was first observed towards the end of the 18th century, but the acid was confounded with benzoic acid, until Bizio, in 1826, showed that it was a distinct acid. It was first investigated by Dumas and Peligot (Annalen, 14, 56).

Occurrence.—In liquid storax, partly free, partly as cinnamyl cinnamate (styracin) ; in tolu and Peru balsams together with benzoic acid and benzyl cinnamate ; in some sorts of gum benzoïn ; in Barbados aloes ; and in the leaves and stalks of *Globularia alypum* and *G. vulgaris*, in the leaves of *Enkianthus japonicus*, and as esters in many varieties of guttapercha.

Formation and Preparation.—It is formed by heating benzaldehyde with acetyl chloride at 120° 130° (Bertagnini, Annalen, 100, 126) :

$$C_6H_5\cdot CHO + CH_3\cdot COCl = C_6H_5\cdot CH:CH\cdot CO_2H + HCl$$
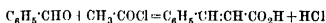
Perkin showed that it might be more readily obtained by heating a mixture of benzaldehyde, acetic anhydride, and anhydrous sodium acetate

$$C_6H_5\cdot CHO + (CH_3\cdot CO)_2O = C_6H_5\cdot CH:CH\cdot CO_2H + C_2H_4O_2$$

(Chem. News, 32, 258 ; Chem. Soc. Trans. 1877, 388). Edeleano and Budishteano (Bull. Soc. chim. 3, [3] 191) state that by heating 1 part of benzaldehyde, 1 part of acetyl chloride, and 3 parts of sodium acetate for 24 hours at 160°, and

subsequently extracting with alkali and precipitating the cinnamic acid with hydrochloric acid, the cinnamic acid is obtained in quantitative yield. The cinnamic acid employed in the preparation of artificial indigo was at first manufactured by this method ; but the process was afterwards improved by Caro (D. R. P. 17467 and 18232 ; Frdl. i. 26), who showed that cinnamic acid could be prepared by heating benzal chloride with dry sodium acetate, thus avoiding the use of the expensive acetic anhydride

$$C_6H_5 \cdot CHCl_2 + 2CH_3 \cdot CO_2Na$$
$$= C_6H_5 \cdot CH : CH \cdot CO_2H + 2NaCl + C_2H_4O_2$$
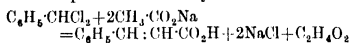
1 part benzal chloride, and from 2 to 3 parts of finely powdered fused sodium acetate (for which potassium acetate or a mixture of the potassium and sodium salts may be substituted) are heated at 180°–200° for from 10 to 20 hours in an autoclave furnished with a mechanical stirrer. The melt is mixed with water, rendered alkaline with caustic soda, and steam-distilled to remove volatile oils, after which the solution in the retort is filtered hot, and the cinnamic acid is precipitated with hydrochloric acid, filtered off after allowing the solution to cool, pressed, and finally purified by recrystallisation from boiling water or alcohol. A method patented by the Farbwerke vorm. Meister, Lucius und Brüning (D. R. P. 18064), in which lead acetate is substituted for sodium acetate, offers no advantages over the foregoing.

Cinnamic acid may be prepared from benzylideneacetone $C_6H_5 \cdot CH.CH \cdot CO \cdot CH_3$, which is readily obtained by the condensation of benzaldehyde with acetone under the influence of dilute caustic soda (Claisen, Ber. 14, 2471). When this compound is oxidised by warming it with sodium hypobromite, it is converted into cinnamic acid (Farbwerke vorm. Meister, Lucius und Brüning, D. R. P. 21162 ; Frdl. i. 28).

By employing substituted benzaldehydes, benzal chlorides, or benzylidene-acetones in the foregoing reactions, substituted cinnamic acids may be obtained.

It may also be prepared from benzaldehyde and malonic acid in the presence of ammonia or amines ; in the place of benzaldehyde the benzylidene compounds of certain amines, such as hydrobenzamide, may be used (Knoevenagel, Ber. 1898, 2692 ; Chem. Zentr. 1898, ii. 695 ; D. R. P. 97735); or by heating benzylidene diacetate with glacial acetic acid and sodium acetate for 10 hours at 160°–180° (Nef, Annalen, 1897, 298, 309).

Cinnamic acid may be extracted from storax by boiling in a retort 1·5 kilos of storax with 2 litres of caustic soda of 24°B. until no more oily drops distil over with the steam. In this process the styracin is hydrolysed, forming sodium cinnamate and cinnamyl alcohol, the latter being volatile with the steam. The aqueous liquid in the retort is separated and the residue repeatedly extracted with boiling water, after which the cinnamic acid is precipitated from the united aqueous solutions by hydrochloric acid and purified by recrystallisation (Beilstein and Kuhlberg, Annalen, 163, 123); Claassen (J. Soc. Chem. Ind. 1897, 932) uses sodium carbonate instead of caustic soda. Precipitated cinnamic acid may be readily freed from adhering resin by recrystallising it from hot light petroleum.

Properties and Reactions.—Forms slender needles or large transparent prisms melting at 133°. Sublimes in absolute vacuum at 108° (Liebermann, Ber. 1900, 33, 2402). Boils at 300° (corr.). If rapidly distilled, it scarcely suffers any decomposition, but by slow heating it is broken up into strylene $C_6H_5 \cdot CH:CH_2$ and carbon dioxide. Sparingly soluble in cold, more readily in boiling water ; easily soluble in alcohol. Forms crystalline salts closely resembling those of benzoic acid. Oxidising agents convert it first into benzaldehyde (distinction from benzoic acid) and afterwards into benzoic acid, the final products when potassium permanganate is used being phenylglyceric acid, benzaldehyde, and benzoic and oxalic acids (Fittig and Ruer, Annalen, 268, 27) When taken internally it is oxidised to benzoic acid, and appears in the urine as hippuric acid. By fusion with caustic potash it yields a mixture of benzoate and acetate It unites with nascent hydrogen to form hydrocinnamic (β-phenyl-propionic) acid ; with bromine to form a dibromide ; and with the hydracids to form β-halogen-hydrocinnamic acids—thus β-chlor-hydrocinnamic acid $C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO_2H$.

Cinnamic acid condenses with hydrocarbons ; thus with benzene and sulphuric acid, it forms phenylhydrindone (Liebermann and Hartmann, Ber 1892, 2124) ; with phenols, phenol itself yielding hydroxyphenylcoumarin (L. and H. ibid. 1892, 957), and with sulphur to form diphenylthiophene. For its *detection, see* Schenk & Burmeister, Pharm. Zeit. 1915, 60, 213 ; Analyst, 1915, 409.

Esters. *Methyl cinnamate.* White crystalline solid ; m p. 36° ; b p. 263°.

Ethyl cinnamate may be obtained direct from benzaldehyde by means of ethyl acetate and sodium (Farb. vorm. Meister, Lucius und Brüning, D. R. P. 53671 ; Eng. Pat. 4969 ; J. Soc. Chem. Ind. 1891, 358 ; Claisen, Ber. 1890, 976). It is a colourless liquid, boiling at 226° (corr.) under 250 mm. (Perkin, Chem. Soc. Trans. 1896, 1228). By heating 2 parts of ethyl cinnamate with 1 part of sulphur at 150°–160° for 8 hours, a yellow odourless compound $C_9H_8S_2O$ is formed, and is suitable for therapeutical purposes (Farb. vorm. F. Bayer and Co. Eng. Pat. 8425 ; D. R. P. 87931 ; J. Soc. Chem. Ind. 1896, 293 ; Kuster, Ber. 1897, 115).

Benzyl cinnamate v. Benzyl benzoate.

Isomeric acids. *Allo*cinnamic acid, m.p. 68°, dimorphous *iso*cinnamic acid, m.p. 42°/58°, have been described, but a discussion as to their constitution cannot be entered into here. (Biilmann (Ber. 1909, 182 and 1443) and Liebermann (ibid. 1027). Cf. Stobbe (Ber. 1911, 44, 2739), who has studied the transformations of *allo-* and *iso*cinnamic acids in the fused and crystalline states.

Substituted cinnamic acids. Of the substitution derivatives of cinnamic acid, the only one of industrial importance is orthonitrocinnamic acid, which is prepared in the manufacture of orthonitrophenylpropiolic acid (*v*. INDIGO, ARTIFICIAL). On a large scale cinnamic acid is first converted by heating with alcohol and concentrated sulphuric acid into ethyl cinnamate. The latter substance, which, being a liquid, is more easily manipulated in the nitration process than the solid cinnamic acid, is run in a thin stream into the calculated quantity of cold

nitrosulphuric acid. The mixture of ortho- and para-nitrocinnamic esters thus formed is dissolved in warm alcohol. On cooling, the para-compound crystallises out, whilst the ortho compound remains in solution. The two ethyl salts are hydrolysed by heating with sulphuric acid. The ortho- acid has also been prepared from o-nitro-benzylidene acetone by warming it with a 3 p.c. solution of sodium hypochlorite (Höchster, Farb. D. R. P. 21162 ; Frdl. 1. 29). In this process the two isomerides are formed in approximately equal quantity.

Orthonitrocinnamic acid

$$C_6H_4(NO_2)CH{:}CH{\cdot}CO_2H$$
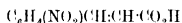
is insoluble in water, sparingly soluble in cold, more readily soluble in boiling alcohol, from which it is deposited in crystals melting at 240°.

The *para- compound* melts at 285°–286°, and is very sparingly soluble in boiling alcohol It cannot be used in the preparation of artificial indigo, and the attempt made to utilise it in the rosaniline manufacture has not proved industrially successful

CINNAMON. The inner bark of shoots of the *Cinnamomum zeylanicum* (Nees), nat. ord *Laurace*, or true laurels According to Percival, it is imported principally from Ceylon , but in part also from Madras, Tellicherry, and, rarely, from Java The bark-peelers select such branches as are 3 years old, and not more than 2 or 3 inches in diameter nor less than half an inch. The bark in drying rolls up into quills, many layers being enclosed in one quill It is used as a condiment, and yields a highly perfumed essential oil (*q v.*), employed in the preparation of chocolate and for purposes of perfumery. Both the bark itself in its powdered state and the oil derived from it are frequently adulterated by cassia (*v* CASSIA).

The value of cinnamon depends upon its content of cinnamaldehyde rather than on the essential oil. A method for the estimation of cinnamaldehyde depends on the coloration developed by treatment with sulphuric acid and isobutyl alcohol (*v*. Fellenberg, Analyst, 1916, 274).

CINNAMON BROWN *v.* AZO- COLOURING MATTERS.

CINNAMON OIL *v.* OILS, ESSENTIAL.

CINNAMON-STONE or **Hessonite.** A gem-variety of garnet of a warm reddish-brown colour (hence the name) and transparent. It is essentially an orthosilicate of calcium and aluminium $Ca_3Al_2Si_3O_{12}$, containing, however, isomorphous replacements of iron, manganese, and magnesium. Brilliant crystals are found in veins in serpentine at Ala in Piedmont, but material of the best gem-quality is found as pebbles in the gem-gravels of Ceylon.

L. J. S.

CINNAMYL COCAINE *v.* COCAINE AND THE COCA ALKALOIDS.

CITARIN. Trade name for sodium anhydromethylene citrate.

CITRAL *v.* TERPENES.

CITRAMALIC ACID *v.* MALIC ACID.

CITRIC ACID $C_6H_8O_7$. *Occurrence.*—This acid commonly occurs in the juice of many fruits, and in the sap of many plants.

Synthesis.—The acid has been prepared artificially by Grimaux and Adam (Compt. rend.

90, 1252). A saturated solution of dichloracetonic acid was neutralised with sodium carbonate, and heated with two molecules of potassium cyanide. The resulting solution of dicyano-acetates was saturated with hydrochloric acid gas, and heated on a water-bath for 15 hours, the citric acid was then separated as calcium citrate by neutralisation with milk of lime. Another synthesis has been effected by Lawrence (Chem. Soc. Proc. 1897, 65), who obtained ethyl citrate by heating together ethyl bromacetate and ethyl oxalylacetate in the presence of zinc.

Properties.—The crystallised acid of commerce has the formula $C_6H_8O_7,H_2O$. The crystals are large prisms belonging to the trimetric system. Their sp gr., according to Buignet, is 1·553 They deliquesce in damp air, and in perfectly dry air slowly lose the whole of their water. Different crystals (probably differently prepared) may lose water at very different rates (Warington, Chem Soc Trans. 28, 928 ; Grosjean, *ibid* , 43, 331) According to Marchand (J. pr Chem 1841, 23, 60), crystals obtained from a saturated boiling solution have the formula $2(C_6H_8O_7),H_2O$ According to a later investigation by Sarandinaki (Ber 5, 110), the crystals from a solution long boiled are anhydrous. Citric acid is optically inactive. The ordinary crystallised acid dissolves in about half its weight of boiling water. Aqueous solutions of various strengths have, according to Gerlach (Zeitsch. anal. Chem. 1869, 295), the following sp.gr at 15° :—

Acid p c	Sp gr.	Acid p c	Sp gr.
1	1 0037	34	1 1422
2	1 0074	35	1 1467
3	1 0111	36	1·1515
4	1·0149	37	1 1564
5	1·0186	38	1·1612
6	1·0227	39	1 1661
7	1 0268	40	1·1709
8	1·0309	41	1·1756
9	1 0350	42	1·1814
10	1·0392	43	1·1851
11	1·0431	44	1 1899
12	1 0470	45	1·1947
13	1·0509	46	1·1998
14	1·0549	47	1·2050
15	1·0588	48	1·2103
16	1·0632	49	1·2153
17	1·0675	50	1·2204
18	1·0718	51	1·2257
19	1·0762	52	1·2307
20	1·0805	53	1·2359
21	1·0848	54	1·2410
22	1·0889	55	1·2462
23	1·0930	56	1·2514
24	1·0972	57	1·2572
25	1·1014	58	1·2627
26	1·1060	59	1·2683
27	1 1106	60	1·2738
28	1·1152	61	1·2794
29	1·1198	62	1·2849
30	1·1244	63	1·2904
31	1·1288	64	1·2960
32	1·1333	65	1·3015
33	1·1378	66	1·3071

A 25 p.c. solution boils at 101·8°, a 50 p.c. solution at 105·8° (Gerlach, J. 1859, 48).

At 15° the solubility of the crystallised acid in alcohol is as follows :—

100 of 80 p.c. alcohol dissolve 87
,,   90 ,,   ,,   ,,   52·85
,, 100 ,,   ,,   ·,   75·90

100 parts of anhydrous ether dissolve 9·1 of the crystallised acid.

According to Buchner (Ber. 1892, 1159), the ordinary hydrated acid melts between 135° and 152°, and the anhydrous acid at 153°. Saltzer (Arch. Pharm. 231, 514) finds that the finely powdered hydrated acid, if slowly heated, becomes anhydrous at 55°, and melts at 160° in this condition.

Decompositions.—When heated to 175°, acetone and carbonic oxide are evolved, the residue is aconitic acid $C_6H_6O_6$; the same acid is formed in small quantity when a solution of citric acid is long boiled (Dessaignes) When heat is continued beyond 175°, an oily distillate appears, which yields crystals of itaconic acid $C_5H_6O_4$. By further heating, itaconic acid is transformed into an uncrystallisable oil, citraconic anhydride $C_5H_4O_4$ Heated with sulphuric acid, carbonic oxide and acetone are given off, the intermediate stage in the reaction being the production of acetone dicarboxylic acid (v Pechmann, Ber 1884. 17, 2542) Thus acetone dicarboxylic acid is also formed in the oxidation of citric acid by potassium permanganate and by the photochemical decomposition of citric acid in the presence of 1 p.c. uranium oxide

Solutions of citric acid are rapidly destroyed by fungi According to F Watts (J. Soc Chem. Ind. 1886, 215), the action of *Saccharomyces mycoderma* on lime juice is to convert the citric acid into carbonic acid and water. According to I. Macagno (Gazz chim ital 11, 443), an alcoholic fermentation in lemon juice does not affect the citric acid, but under the influence of bacteria the citric acid disappears, and acetic and propionic acids are formed.

Salts.—Citric acid is tribasic, and forms in consequence three classes of salts The salts with the alkali metals are readily soluble in water ; the neutral salts of the alkaline earths are only sparingly soluble

Calcium citrate $Ca_3(C_6H_5O_7)_2.4H_2O$ does not lose water at 100° When precipitated in a crystalline state its solubility in water is 1 in 1180 at 14°, and 1 in 1730 at 90° 100°. When thrown down in an amorphous condition, the solubility is greater, 1 in 707 at 18°, and 1 in 1123 at 100° (Chem. Soc. Trans. 28, 939)

When a solution of citric acid contains a ferrous, ferric, or aluminium salt, in not too great proportion, it may be made strongly alkaline with potash or soda without producing a precipitate. Such a solution may also be boiled with chalk without precipitating iron or aluminium, although a large part of the citric acid falls as calcium citrate. (With tartaric acid in the place of citric, iron is to a small extent precipitated by chalk in the cold, and entirely on boiling.) If, however, the ferric salt bears a large proportion to the citric acid, the whole is precipitated by chalk, even in the cold (Chem. Soc. Trans. 28, 990).

Derivatives.—Methylenecitric acid is obtained

by heating citric acid with four times its weight of polymeric formaldehyde at 140°–160°, and allowing the melt to crystallise. It is tolerably stable towards acids, but is decomposed by alkalis with elimination of formaldehyde. Its di-sodium salt is known as 'citarin.' It is used as a disinfectant for the urinary passages (Ch. Fab. auf. Act. vorm. E. Schering, U.S. Pat. 699422 ; J. Soc. Chem. Ind. 1902, 791).

Monophenetidenecitric acid is obtained by heating 42 parts of citric acid with 27·5 parts of *p*-aminophenetol for some hours at 100°. The product is dissolved in caustic soda, and the acid precipitated with hydrochloric acid. Diphenetidenecitric acid is obtained similarly. They are medicinal substances, acting energetically as precipitants without producing secondary symptoms (Farb von Heyden-Nachfolger, Eng. Pat 1254 , J. Soc Chem Ind. 1895, 385).

Detection.—Citric acid is best recognised when in a pure state by its yielding on heating an oily sublimate, which afterwards crystallises (itaconic acid). A solution of citric acid, neutralised with ammonia, gives no precipitate in the cold with calcium chloride, except after long standing , but on boiling, calcium citrate is precipitated. Calcium citrate, precipitated in the cold, is freely soluble in solution of ammonium chloride, and is precipitated therefrom on boiling Alkali citrates do not reduce silver salts on boiling, as tartrates do, or only to a trifling extent.

Kämmerer (Zeitsch. anal. Chem. 8, 298) recommends the detection of citric acid by the formation of a crystalline barium salt. To the free acid, or to the alkali salt, excess of barium acetate is added, and the whole heated on a water-bath for several hours ; the barium citrate

$$Ba_6(C_6H_5O_7)_4.7H_2O$$
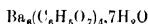
will then be found in microscopic monoclinic prisms

Déniges (Compt. rend. 130, 32) adds to the solution ¼ of its volume of a reagent obtained by dissolving 5 grams of mercuric oxide in 20 c.c. of conc sulphuric acid, and 100 c.c. of water. The solution is heated to boiling, and, if citric acid is present, a white precipitate is obtained on the addition of a few drops of a 2 p c solution of potassium permanganate.

Another method is to add potassium permanganate to the solution until it is pink. If a precipitate is formed, or a brown colour produced, ammonium oxalate is added until it is destroyed. On adding bromine water a white precipitate is obtained, which, on the addition of alkali, gives the characteristic smell of bromoform (Stahre, J. Soc. Chem. Ind. 1896, 53 ; Wöhlk, Zeitsch. anal Chem. 1902, 77).

The tests for adulteration will be given at the close of this article.

Estimation.—When the quantity of citric acid in a solution is determined by alkalimetry, phenolphthalein should be used as the indicator ; in coloured solutions red-brown turmeric paper (Thomson, J. Soc. Chem. Ind. 1887, 195) has been recommended. If neutral litmus paper is used, the alkali must be standardised with citric acid. The quantitative determination of citric acid by precipitation as calcium citrate will be described under the analysis of lemon juice.

Citric acid in milk and wine. Citric acid is

present in milk and wine, and as it occurs in small quantities in most wines, adulteration with a small quantity of citric acid cannot be detected (Hubert, Ann. Chim. anal. 1908, 139). It may be detected in milk by taking 10 c.c. of milk, 2 c.c. of sodium metaphosphate, 3 c.c. of mercuric sulphate solution, and filtering. Half of the filtrate is mixed with 0·5 c.c. of 10 p.c. solution of manganese sulphate, and boiled. To this 4 drops of a 2 p c. solution of potassium permanganate is added, and the solution again boiled. This is repeated, and the liquid decolourised by a drop of hydrogen peroxide A precipitate or an opalescence indicates the presence of citric acid. This method may be used quantitatively (Dengès, Chem. Soc Abstr. 1902, ii. 365; v also Scheibe, ibid 1891, 1276). It may be detected in wine by the method of Spica (Gazz. chim ital 31, [2] 61) A portion of the wine is evaporated to a syrup and extracted with alcohol. This is nearly neutralised with alcoholic potash, and the potassium bitartrate filtered off The filtrate is then neutralised with more potash, and the precipitate is filtered off, dried, and heated in a small tube with sulphuric acid, until it goes brown. It is then diluted, made alkaline with caustic potash, and sodium nitroprusside added. A red colour indicates the presence of citric acid. Favrel (J Soc Chem Ind 1908, 637) evaporates 100 c c. of wine to dryness, dissolves the residue in 7 c c. of boiling water, and adds 35 c.c. of 90 p c. alcohol A solution of calcium acetate (0·4 gram in 5 c.c of water) is added, and the precipitate filtered When dry it is transferred to a test-tube, 3 c.c of sulphuric acid added, and the whole heated to 80°–90° for 2 minutes. The solution is cooled and extracted with ether White crystals are obtained, giving a violet-red colour with ferric chloride, the colour being discharged by mineral acids (For other methods and quantitative estimation, v. Williams, Analyst, 14, 25; Devarda, J. Soc. Chem. Ind. 1904, 273; Klinger and Bujard, Chem. Soc. Abst 1893, ii. 54; Schindler, Chem Zentr. 1902, ii. 1016; and Robin, Ann. Chim. anal. 1904, 453.)

Gowing-Scopes finds that a mixture of equal weights of mercuric nitrate, manganese nitrate and nitric acid reacts with citric acid, yielding a precipitate after prolonged boiling which is exactly six times the weight of citric acid present. The method gives good results in presence of tartaric, succinic and other organic acids, but with malic and lactic acids the results are high (Analyst, 1913, 12).

RAW MATERIAL.

Citric acid is prepared from the fruit juice of three species of *Citrus*—the lemon, bergamot, and lime; the first of these is the principal source of citric acid. Concentrated lemon juice is chiefly imported from Sicily; a very little comes from Naples or Sorrento. Concentrated bergamot juice is prepared in Calabria, and exported from Messina. Concentrated lime juice is imported from Montserrat and Dominica. The lemon juice from Sicily is prepared by pressing the inferior fruit, from which the rind has previously been removed for the manufacture of essence. The so-called 'single' juice

is then boiled down till its sp.gr. equals 60° on the citrometer (sp.gr. 1·24); it then forms a dark-brown, rather syrupy liquid.

Lemon juice has its greatest acidity early in the season (November). The juice of the fine fruit, exported as lemons, has a sp.gr. 1·03–1·04; it contains free acid equal to 11–13 oz. of citric acid per gallon. The inferior fruit pressed in Sicily yields a juice containing at the beginning of the season about 9 oz. of free acid per gallon, and at the end of the season a good deal less.

There are other differences between the juice of fine lemons pressed in England, and the Sicilian juice employed for the manufacture of citric acid. The former contains very little combined organic acid, only about 2·5 p.c. of the total organic acid (free plus combined) present. In unconcentrated Sicilian juice the combined acid is about 7–9 p.c. of the total. Again, the English pressed juice contains hardly any organic acid save citric, only about 1 p c. of the total organic acid being unprecipitable as calcium citrate In Sicilian juice about 8 p.c. of the total organic acid is unprecipitable as calcium salt

The concentrated lemon juice from Sicily is reckoned of standard quality when its sp.gr. is 1 24, and its acidity is equal to 64 oz. per gallon of nominal citric acid. In dealing with trade analyses it must, however, be borne in mind that the 'crystallised citric acid' of a trade certificate is not the crystallised acid of commerce, but an acid containing only half the actual amount of water, an acid, in fact, having the atomic weight 201 instead of 210 :

$$C_6H_8O_7,H_2O$$

No reason can be given for this practice, which should certainly be abolished In the present article all quantities of citric acid will be expressed in terms of the common crystallised acid

The concentrated lemon juice from Sicily contains pretty uniformly 7–8 oz. per gallon of combined organic acid, equal to about 10 p.c. of the total organic acid (reckoned as citric) present. Of the total organic acid about 10 p.c. is not precipitable as calcium salt, and is therefore not citric acid ; this proportion is, however, by no means constant. Purchases of lemon juice are unfortunately still made on the basis of acidity, and not on the amount of precipitable acid present. Analyses of 895 pipes of concentrated lemon juice by Grosjean have been published (Chem. Soc. Trans. 43, 333). The average proportion of precipitable acid was 99·2 p.c. of the free acid, but the range of variation was considerable, individual parcels of juice giving 81·1, 85·8, and 103·6 p.c.

Concentrated Bergamot juice has a similar sp.gr. to lemon juice, but a lower acidity ; it generally contains free acid equal to about 51 oz. of citric acid per gallon. The quantity of combined organic acid is apparently similar to that in lemon juice, namely, 7–8 oz. per gallon ; but the proportion of combined to total is higher, 12–13 p.c. The proportion of unprecipitable acid is about 13 p.c. of the total. Grosjean's analyses of 90 pipes of bergamot juice show a mean of 98·4 of precipitable acid for 100 of acidity, the extremes being 95·4 and 101·4.

The unconcentrated **Lime juice** of Montserrat has a mean sp.gr. of 1·036 ; it contains, according to Conroy (Pharm. J. 1883, 606), an average of 7·84 p.c., or 12·54 oz. per gallon of free acid. The extremes observed were 6·70–10·05 p.c., equal to 10·7–16·1 oz. per gallon. The juice yields 0·43 p.c. of ash. It contains only a trace of sugar. Warington found the combined acid in two samples 5 p.c. of the total ; 10 p.c. of the total acid was not precipitable.

Concentrated lime juice is a viscid liquid, sp.gr. 1·32, and with an acidity averaging about 94 oz. of citric acid per gallon. The combined acid is about 8·9 oz per gallon. The unprecipitable acid is about 10–14 p.c. of the total. The precipitable acid bears a lower proportion to the free than is the case with either lemon or bergamot juice, the published analyses showing a mean of 93·8 of precipitable acid for 100 of free.

The nature of the organic acids, other than citric, present in lemon, bergamot, and lime juice has not been determined A little formic acid and acetic acid have been detected in concentrated juice, but the principal acids other than citric are clearly non-volatile and have soluble calcium salts The acids most probably present are malic and aconitic

Besides lemon juice, some crude **Calcium citrate**, prepared in Sicily by precipitating lemon juice with chalk, is exported into England. It contains about 64 p c. of citric acid.

METHODS OF ANALYSING JUICE AND CITRATE.

1. *Acidity.*—The commercial analysis of juice is confined to the determination of acidity. It is most important that the alkali (sodium hydroxide) used should be actually standardised with citric acid, and the same indicator employed in standardising as in subsequent analyses. Powdered crystals of citric acid are taken, water carefully determined in one portion, while another is used for standardising the alkali In determining water, the powdered acid should be heated for some hours at about 60° before exposing it to 100° ; if this is not done, the acid will melt, and lose the rest of its water with great difficulty. Warington recommended delicate litmus paper for determining the neutral point. F. Watts has since employed films of turmeric tincture on a white tile (J. Soc. Chem. Ind. 1886, 214). Thomson recommends red-brown turmeric paper.

2. *Combined organic acids.*—The juice is neutralised with a known quantity of standard alkali, evaporated to dryness in a platinum basin, the residue gently ignited, the black ash treated with a known quantity (excess) of standard sulphuric acid, the whole boiled and filtered. The amount of unneutralised acid is then determined with alkali. We have now the neutralising power of the ash in terms of alkali ; by subtracting the alkali added when neutralising the juice, we obtain the amount of alkali corresponding to the bases of the organic salts, which became carbonates on ignition. From the amount of these bases their equivalent in combined citric acid can be calculated.

3. *Precipitable citric acid.*—This is for the manufacturer the only trustworthy method of analysis, but is, in fact, seldom adopted. War-

ington proceeds as follows : 15–20 c.c. of unconcentrated juice, or about 3 c.c. of concentrated juice, are exactly neutralised with sodium hydroxide, the solution (about 50 c.c.) is brought to boiling in a salt-bath, and a measured quantity of calcium chloride solution, known to be rather more than sufficient for all the organic acids present added. After boiling for half an hour, the precipitate is collected on a small filter, and washed with hot water. The filtrate and washings are then concentrated to 10 c.c. and the solution finally neutralised with a drop of ammonia. The second precipitate is collected on a very small filter, the filtrate being used for getting the precipitate on to the paper, which is finally washed about five times with a little hot water. The precipitates in their papers are then burnt at a low heat in a platinum basin, and the neutralising power of the ash determined with standard hydrochloric acid and alkali. The amount of citric acid which the base is equivalent to can then be calculated, three molecules of base being reckoned as equivalent to one molecule of citric acid.

4. *Analysis of calcium citrate.*—The excess of chalk present is first determined by boiling about 4 grams with dilute standard hydrochloric acid in a covered beaker, and then adding standard alkali till feebly alkaline Two grams of the citrate are then gently ignited in a covered platinum crucible, and the neutralising power of the ash determined by solution in standard hydrochloric acid and titration with alkali. By deducting from the neutralising power of the ash that due to the chalk previously determined, we find the amount of base which has to be calculated as citrate. This method presupposes that citrates are the only organic salts present. If it is preferred, the citrate may be dissolved in hydrochloric acid, the solution boiled, neutralised with soda, the calcium citrate precipitated by boiling in the salt-bath, and its quantity determined as in the case of juice.

The information here given respecting juice, calcium citrate, and the methods of their analysis, will be found in greater detail in Chem. Soc. Trans 28, 925 ; 43, 331 ; *v.* also Ulpiani and Parrozzani (Chem. Soc Abstr. 1907, ii. 57) ; Shica (Analyst, 1910, 35, 519) ; Barboni (*ibid.* 1913, 65).

PROCESS OF MANUFACTURE.

The manufacture of citric acid from concentrated lemon juice is extremely simple. A proper quantity of whiting (levigated chalk) is mixed with water, and heated by steam in a wooden vat provided with a revolving agitator ; the concentrated juice is then slowly pumped in, care being, of course, taken that the whiting is finally in small excess. The liquor never becomes neutral, however long boiling may be continued, or however great is the excess of whiting present ; the adjustment of juice and whiting is therefore effected by ascertaining if the liquor effervesces with more whiting, or the precipitate effervesces with more juice. The amount of unneutralised acid is about 1–2½ p.c. of the original acidity of the juice. Pure citric acid is readily neutralised by whiting, malic and aconitic acids are not; the final acidity is thus possibly due to the presence of these acids. Citric acid, however, is not

neutralised by chalk if phosphates, and especially ferric phosphates, be present; this fact will also explain the result. It is not advisable to neutralise completely by the use of lime, as vegetable impurities are then thrown down which are afterwards difficult to separate.

The precipitated calcium citrate is washed with hot water on a filter It is next brought by the addition of water to the state of thin cream, and decomposed, with constant agitation, by the addition of a small excess of sulphuric acid (sp gr. 1·7). The occurrence of an excess of sulphuric acid is known by the liquor affording a precipitate with a strong solution of calcium chloride after some minutes' standing

The citric acid liquor is then separated from the gypsum, which is washed on a filter The liquor is evaporated in shallow leaden baths by steam heat Much gypsum is at first deposited, from this the clear liquor is run off and further concentrated. When strong enough to crystallise, the hot liquor is run into a wooden tub provided with an agitator, and the liquor is kept in constant motion while cooling, by this process, known as 'granulation,' the citric acid is obtained as a crystalline powder. The mother liquor is again concentrated, and 'salt' again obtained by granulation The process may be repeated a third time The liquor is then too dark and impure for further crystallisation, and is known as 'old liquor' The granulated citric acid when drained, and, if necessary, slightly washed, is redissolved, decolourised by heating with animal charcoal (previously freed from phosphates by hydrochloric acid), again concentrated to the crystallising point, and poured into leaden trays about 3 inches deep; the crystals here formed are the citric acid of commerce Citric acid thus prepared always contains a trace of lead, and often particles of metallic lead, probably due to the plumbers repairing the vessels. To free the acid from lead, the process usually adopted is to pass sulphuretted hydrogen through the solution after the first crystallisation, filter, and then recrystallise the citric acid in lead-free vessels.

The 'old liquor' is diluted with water, and the citric acid it contains precipitated with an excess of whiting, exactly as in the case of the original juice. The liquor is never neutralised by the whiting; this may be either due to aconitic acid formed during the heating of the citric acid liquors, or to the presence of ferric or aluminic phosphate derived from the whiting.

Any considerable excess of sulphuric acid in the liquors, or any overheating, must be avoided, as occasioning decomposition of citric acid The presence of iron or aluminium in the whiting also occasions loss, as citric acid holding iron or aluminium in solution is not precipitated by calcium carbonate. In consequence of the non-precipitation of iron or aluminium from citric solutions by whiting, the citric liquors of the factory remain nearly pure, however long the work may have been continued, a result very different from what happens in the case of tartaric acid; the purity of citric-acid liquors is however obtained at the expense of some loss of citric acid. In a well-conducted factory the total loss during manufacture will amount to 12–15 p.c. of the citric acid in the juice.

A method has been patented (Fancheux and

Boissière, Eng. Pat. 11991; Fr. Pat. 338735; J. Soc. Chem. Ind. 1904, 680) by which the crude calcium citrate is purified by passing hot gases over it, so as to roast it superficially.

Citric acid is also produced by the fermentation of carbohydrates, glycerol, and analogous substances under the influence of certain fungi, named *citromyctes* (Wehmer, Eng. Pat. 5620; D. R. P. 72957, J Soc. Chem. Ind. 1894, 275). To prepare the organisms, a sugar solution containing 2 5 p.c of citric acid is allowed to stand for a few days. The growth formed on this solution is introduced into sterilised sugar, where it develops The pure culture prepared in this way is then introduced into large vessels containing sugar solution, in which are dissolved small quantities of ammonium nitrate, dipotassium phosphate, and magnesium sulphate; the liquid is then allowed to remain at the ordinary temperature for 8–14 days At the expiration of that time, the liquid contains a certain amount of citric acid, so that it can be directly employed for lemon juice The acid can be isolated, preferably as calcium citrate by adding calcium carbonate to the liquid Other moulds, such as *Mucor piriformis*, which grows on putrefying fruit, specially on pears and apples, may be employed (D. R P. 91891, v. also Maze and Perrier, Compt. rend. 139, 344).

Estimation of lead in citric acid. Forty grams of the sample are dissolved in water, pure strong ammonia added in slight excess, the liquid cooled and diluted to 120 c c For a preliminary experiment 10 c c are taken, diluted to 50 c c in a Nessler tube, and one drop of ammonium sulphide added, the colour determines what volume should be taken; it varies from 5 to 50 c c. Having repeated this with the volume of liquid thus indicated, the tint has to be matched with that from the pure solution A volume of pure ammonium citrate solution identical with that taken of the acid under examination is mixed with a measured quantity of slightly acid lead nitrate solution, containing 0 1 gram metallic lead per litre A drop of ammonium sulphide is added, and various solutions are made up until the colour obtained matches that from the acid under examination If iron or copper is present in any quantity, a drop of solution of potassium cyanide is added before the ammonium sulphide which prevents them interfering with the reaction. The standard of purity suggested is that lead is not to be present to a greater extent than 5 parts per million (Warington, J. Soc. Chem Ind. 1893, 97; v. also Tatlock and Thomson, Analyst, 1908, 173).

Another method is that of Buchet (J. Soc. Chem Ind. 1892, 848) To estimate the metallic lead, 200 grams of acid are dissolved in three times its weight of water, and a slight excess of ammonia added. After 24 hours the liquid is decanted, and the residue collected on a filter, carefully washed and dissolved in nitric acid. The lead is then precipitated as sulphate, and estimated as such. To determine the combined lead, the ammoniacal solution is first acidified with hydrochloric acid, the lead precipitated as sulphide, converted into sulphate, and weighed as such.

Adulteration.—Citric acid is at times adulterated with tartaric acid. To detect adulteration,

Cailletet (Chem. Soc. Trans. 36, 674) adds 1 gram of the powdered acid to 10 c.c. of a cold saturated solution of potassium dichromate. If the solution remains unchanged in colour for 10 minutes, tartaric acid is absent. If tartaric ·is present, the solution becomes brown. Pusch (J. Soc. Chem. Ind. 1885, 552) places 1 gram of the acid in a test-tube with 10 grams of pure oil of vitriol. The test-tube is placed in a water-bath, and kept at 100° for 1 hour. If citric acid only is present, the colour is lemon-yellow. If tartaric acid is present, the colour becomes brown. Both these tests are very delicate, and readily show 1 in $\frac{1}{2}$ p.c. of adultera-tion. Piñerua (Compt. rend 124, 291) puts 0·05 gram of the substance in a porcelain basin, and adds 10–15 drops of a reagent made by dissolving 0 02 gram of β-naphthol in 1 c c of concentrated sulphuric acid If citric acid alone is present, a blue colour is formed, un-changed on heating, which on dilution gives a nearly colourless or a slightly yellow liquid If tartaric acid is present, the colour on heating changes to green, and on dilution to a reddish-yellow. Denigès adds a small quantity of the acid to a solution of resorcinol in dilute sulphuric acid, and heats to 115°–140°. If tartaric acid is present, a violet-red colour is formed. If sugar is present, or other bodies blackened by sulphuric acid, the acid is precipitated as its lead salt, and then tested (J Pharm Chim 1895, i 586) Crismer (Chem Soc. Abstr 1892, 546) adds 1 gram of the acid to 1 c c. of ammonium molybdate solution (10 p c) and 2 to 3 drops of hydrogen peroxide solution ($\frac{1}{4}$ to $\frac{1}{2}$ p.c.), and heats at 100° for 3 minutes. If citric acid alone is present, the yellow colour given by the molybdate is unaltered ; whilst if tartaric acid is present, a beautiful blue colour results. This test detects 1 mgm. of tartaric acid in 1 gram of citric acid. Spindler has modified Denigès' mercuric sulphate method (q v), and uses potassium dichromate instead of permanganate If citric acid alone is present, a yellow precipi-tate is obtained ; the presence of tartaric acid is indicated by a change of colour to green, due to reduction. Tartaric acid may also be detected by adding a little solution of potassium acetate to a strong solution of the citric acid, and stirring.

The quantity of tartaric acid in an adul-terated sample may be determined by adding 10 p.c. of potassium chloride to a strong solution of the acid, and precipitating the tartaric acid with citrate or acetate of potassium, with the precautions described under estimation of tar-taric acid.

CITRIC ACID FERMENTATION v. FERMEN-TATION.

CITROCOLL. Trade name for neutral aminophenacetin citrate.

CITRON, OIL OF, v OILS, ESSENTIAL.

CITRONELLA OIL v. OILS, ESSENTIAL.

CITRONINES v. AZO- COLOURING MATTERS.

CIVET. An odoriferous substance resem-bling musk or ambergris, obtained from the pouches situated between the anus and genital organs of *Viverra civetta* of N. Africa, *V. Zibetha* of Asia, and *V. Malaccensis* of Java. Is of the consistence of honey, and of a yellowish or brown colour. Contains stearin, olein, mucus, resin, volatile oil, and yellow colouring matter (J.

Pharm. 1824, 537). (For analyses of civet, *see* Charabol and Hébert, Bull. Soc. chim. 1910, 7, 687.) Civet melts at about 36°, and contains from 50 to 70 p.c. of fatty acids, and should have a saponification value of about 180°, and should have not more than 1 p.c. of ash.

It has been inferred that the musk aroma of civet is due to a ketone, *muskone*, present in musk, but according to Sack (Chem. Zeit. 1915, 39, 538), it is caused by a specific ketone, *Zibetone* $C_{17}H_{30}O$, of a pleasant musk-like odour, which may be obtained pure by decomposition of the crystallised semicarbazone. Its oxime crystallises in white needles, m.p. 92°. *See* MUSK.

CIVETONE or **ZIBETONE** v MUSK.

CLAUSTHALITE v. SELENIUM.

CLAVICEPSIN v ERGOT

CLAVIN v. ERGOT

CLAY. (*Argile*, Fr ; *Thon*, Ger.) The term ' clay ' is ordinarily used to denote certain earths, the chief characteristic of which is that of plasticity when wet, and which have the property of baking to a hard, stone-like mass when heated to full redness. Clay is a hetero-geneous mixture of certain hydrated aluminium silicates, with particles of quartz, felspar, mica, &c, resulting from the decomposition of various siliceous minerals, the chief source being the felspars of granite rocks. These hydrated aluminium silicates form the essential basis of all clays, and are known as *clay substance* or *clay base*. They are all decomposed by hot concentrated sulphuric acid (*infra*), whilst the other ingredients mentioned above are affected only slightly or not at all. The method of so-called ' rational analysis ' is based on this action, and it has been found that when so treated, the great majority of clays give a clay substance approximately of the composition represented by the formula $Al_2O_3 \cdot 2SiO_2, 2H_2O$. This corresponds with the composition of the rare crystalline mineral *kaolinite*, and, conse-quently, it has often been assumed that all clays contain kaolinite as their clay base. It has, however, been shown that the clay substance, in some cases, does not correspond in composition with the above formula, and it is now generally accepted that other hydrated aluminium silicates may be present in clays, forming part, and in some cases the whole, of the clay base. Various investigators have attempted to define these substances, and to show that they correspond in composition with certain silicates, such as allophane $(Al_2O_3 \cdot SiO_2, 5H_2O)$, pyrophyllite $(Al_2O_3 \cdot 4SiO_2, H_2O)$, halloysite $(Al_2O_3 \cdot 2SiO_2, 2H_2O + Aq)$, pho-lerite $(2Al_2O_3 \cdot 3SiO_2, 4H_2O)$, &c

It has been suggested by J. W. Mellor (Trans. Eng. Ceramic Soc. pt. 1, 8) that the term *kaolinite* should be restricted to the compara-tively rare crystalline mineral, and that the amorphous clay substance of similar compo-sition $(Al_2O_3 \cdot 2SiO_2, 2H_2O)$ should be called ' clayite.'

The same investigator points out that this latter substance occurs in clays in non-crystal-line or amorphous granules, which, however, sometimes show faint polarisation phenomena. Practically all clays contain more or less free silica, undecomposed or partially decomposed felspar, and mica, and they vary in composition

through a wide range, differences in composition being brought about partly as a result of different origins, and partly by differences of deposition, &c. The commoner varieties of clay generally contain a considerable percentage of oxide of iron, and small percentages of calcium, magnesium, and titanium salts.

According to Washington (J. Amer. Ceram. Soc. 1918, 1, 405) clays are composed of four minerals corresponding to generalised formulæ, viz. *kaolinite* $(Al_2O_3,2SiO_2,2H_2O)$, *orthoclase* $(K_2O,Al_2O_3,6SiO_2)$, albite $(Na_2O,Al_2O_3,6SiO_2)$, *anorthite* $(CaO,Al_2O_3,2SiO_2)$, *limonite* (Fe_2O_3, H_2O) with, in some cases, *muscovite* $(K_2O,2H_2O, 3Al_2O_3,6SiO_2)$. The proportions of the several minerals may be calculated from the ultimate chemical analysis. The lime, soda, and potash are first calculated to the felspars, and the alumina and silica required for these are deducted from the total. The iron oxide is calculated as limonite. Any surplus alumina is calculated as kaolinite, and any surplus silica is regarded as quartz (*see below*).

Clays may be divided broadly into two classes : residual clays and sedimentary clays Residual clays are the insoluble residue left from the breaking down and decomposition of rock masses containing certain aluminium silicates (chiefly felspathic minerals), and they are found overlying or adjacent to the rock mass from which they are formed. These residual clays usually present a gradual change in mineral character from the finer or purer portion nearer the surface to the mixture of clay and undecomposed rock which lies in contact with the rock mass. The decomposition of the mineral silicates may be brought about by carbonic acid in the surface waters ; but many of them are acted on by water alone, and although this action proceeds very slowly, it may account for the gradual decomposition of the felspathic rocks and the formation of clay. The alkalis of the felspars combine with the free silica formed in the decomposition, and with the carbon dioxide contained in the percolating water, forming soluble salts which are more or less completely washed away. In some cases the decomposition of the mineral silicates may have been brought about by the action of gases, and it has been shown by J. H. Collins (Min. Mag. 1887, 7) that when felspar is exposed to the action of hydrofluoric acid, hydrated aluminium silicate is formed, mixed with soluble potassium fluoride, whilst silica is deposited on the sides of the tube in which the reaction takes place. Residual clays, as a rule, contain a smaller percentage of oxide of iron and organic matter than sedimentary clays, and are consequently lighter in colour both before and after baking.

Sedimentary clays are formed by the transportation and redeposition in water of residual clays, and clays so formed may be again transported and redeposited in the same way, so that they may have no direct relationship to the rock formation on which they lie. Sedimentary clays belong to all geological ages, from the present to the Cambrian, and are of varying degrees of hardness, from the soft drift which may be dug with a spade to the hard clay shales of the older formations, which require to be blasted. These clays are always roughly stratified in structure, and show considerable variations in general character and composition throughout their mass, owing to the varying conditions under which they were deposited. The harder varieties of clay are readily converted into the plastic form by grinding with water, or by *weathering*, and they are now largely used for the making of bricks, &c., where formerly only the softer surface clays were used. When breathed upon or moistened, clays usually emit a peculiar odour known as argillaceous. This characteristic is more marked in the sedimentary than in the residual clays, and may possibly be connected with the contained organic matter.

Plasticity is an essential property of all clays in the moist condition, but this quality varies greatly in different clays. The presence of organic matter, finer grinding of the particles of the clay, ' ageing ' in the moist condition and ' weathering,' all tend to increase the plasticity, but no entirely satisfactory explanation of the cause of plasticity has yet been put forward. Clay loses practically the whole of its hygroscopic water when dried at 100°, and it contracts and loses its plasticity at the same time, becoming hard and brittle. On being soaked or ground in water, however, it becomes soft and plastic again. The chemically combined water is not driven off until the clay is heated to redness, the temperature of the dehydration, in the case of ordinary clay, being probably between 480° and 600°. Clay that has been heated to this temperature will not again become plastic on being ground with water, so that it is evident that the plasticity of a clay is dependent upon some physical or chemical condition, which is destroyed on heating to about 500°. When clays are heated to a higher temperature (generally about 900°), they contract more or less and become hard, compact, and stone-like, and at higher temperatures still they become vitreous and ultimately fuse. The purest varieties of china clay (which approximate to the composition of kaolinite) fuse at a temperature of about 1830°, and other clays fuse at lower temperatures, according to the nature and percentage of the various impurities contained. The chemical impurities which chiefly affect the fusibility of a clay are the salts of magnesium, calcium, iron, sodium, and potassium. Richter first pointed out that chemically equivalent amounts of the oxides of these substances exert equal influences on the fusibility of a clay. The presence of free silica (quartz sand) tends to raise the fusion point of clays containing a considerable percentage of these bases, but it has an opposite effect on the purer china clays. In the manufacture of pottery ware of all kinds, the firing temperature depends upon the chemical composition of the clay (which determines the fusibility) and upon the result required. For example, in the manufacture of porcelain, where the resultant ware must be non-absorbent or vitreous, the firing temperature ranges from about 1250° to 1550°, according to the chemical composition of the clay mixture or *body* used, whereas in the manufacture of ordinary white earthenware, where a porous or non-vitreous ware is desirable, the firing temperature ranges from about 1150° to 1250°.

The colour of fired clay, *i.e.* clay that has

been heated to a temperature of over 900°, depends upon the impurities present, and upon the character of the firing gases. The purer kinds of residual clays fire to a whitish mass, but all other clays become more or less strongly coloured, the tint being determined generally by the percentage of iron oxide present. Iron may be present in clays in various combinations, such as ferric oxide (Fe_2O_3), hydrated ferric oxide ($2Fe_2O_3,H_2O$), ferrous carbonate ($FeCO_3$), and more rarely magnetic oxide (Fe_3O_4), but in firing in the ordinary way all these salts are converted into ferric oxide. Some clays contain a considerable amount of iron pyrites disseminated through the mass in small grains, and these clays are often troublesome in use, as the sulphide is not so readily converted into oxide in the ordinary firing process. Moreover, the sulphide on weathering with the clay gives rise to soluble sulphates which are detrimental. In the yellow and brown surface clays and red-firing shales, the iron is present in the form of ferrous carbonate, which, together with the organic matter present, produces the natural grey colour of these shales. In ordinary clays, and with an oxidising atmosphere, 1–2 p.c. of iron oxide produces a buff colour, 2–4 p.c. a salmon colour, and above 4 p.c. a red colour, which becomes darker as the percentage of iron increases. The presence of other impurities, however, modifies the colour produced by iron oxide considerably, and this is especially the case when a large percentage of lime or magnesia is present.

Some clays (commonly called marls) contain from 15 to 30 p.c. of lime, and although they may also contain as much as 6–8 p.c. of iron oxide, they fire to a light-yellow or buff colour. Such clays are largely used for making the well-known yellow facing bricks, which were at first made chiefly from the marls of the Thames basin, the Paris basin, &c., and are now made from artificially prepared mixtures of clay or chalk and limestone. The presence of certain soluble salts (chiefly sulphates of calcium or magnesium) in clays often produces serious discolouration on firing, owing to the deposition of these salts on the surface during the drying and firing of the ware. To prevent this action, it is usual to mix with the clay barium carbonate, to combine with the whole of the sulphuric acid present, and so convert the soluble salts into insoluble ones. When clays are fired in a reducing atmosphere, the red ferric oxide is converted into blue ferrous oxide, and the resultant ware is consequently bluish in colour. Blue bricks are made from certain clays, containing generally from 6 to 10 p.c. of iron oxide by firing in this way.

The presence of clay in soils exerts an important action on the growth of plants. Ammonia is retained by clay in such a manner that it cannot be removed except by an excessive amount of washing; in fact, clay will remove ammonia and many organic substances from manure, and still retain them in a form readily available for plants.

Kaolinite $Al_2O_3\cdot2SiO_2,2H_2O$. A comparatively rare crystalline mineral which occurs in Anglesey, in Colorado, and a few other localities in the form of minute hexagonal plates, having a perfect basal cleavage, and belonging to the monoclinic system. Kaolinite was formerly

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supposed to form the base of all clays, but this view is no longer held, and the term should be restricted to the crystalline mineral described above.

Kao-lin, China clay. The Chinese term ' kao-lin ' (literally meaning ' high ridge ') was applied to the white earth from which porcelain was made, and it corresponds to the English china clay, so called because it is used for the making of ' china,' or porcelain. These terms are now applied to all the purer residual clays which contain a high percentage of hydrated aluminium silicate ($Al_2O_3\cdot2SiO_2,2H_2O$), and which consequently give on analysis 33–40 p.c. alumina (Al_2O_3), 45–60 p.c. silica (SiO_2), 11–14 p.c. water, with very small percentages of iron oxide, soda, potash, lime, magnesia, &c. Clays of this class are worked in Cornwall and Devon, at St. Yrieix near Limoges, Zettlitz in Bohemia, in the United States, in South Africa, &c. As mined, the clay generally contains a large percentage of quartz-sand and mica, and it is refined by washing. In Cornwall the china clay is usually the result of the weathering of pegmatite, and the felspar of the parent rock is often decomposed to a depth of 60 to 100 feet. In this condition it is known as *china clay rock*, and the workman breaks down the crumbling surface with a pick and then directs a stream of water over this to wash down the material, which is passed into tanks where the suspended matter settles out, the quartz, clay, and mica being deposited according to the sizes of the particles, and so separated from each other. The china clay is allowed to dry to a stiff paste in the tanks, and is then removed to the drying kilns, where it dries until it can be cut into blocks ready for shipment. It is a soft, friable, sectile, white substance, showing irregularly shaped granules under the microscope, and possessing only a moderate plasticity when mixed with water. *Cf.* Coon, Trans. Eng. Ceramic Soc. 1910–1911, 10, 81. China clay is used in the manufacture of porcelain and white earthenware, in paper making, and the *filling* of calico, and also in the manufacture of alum, aluminium sulphate, and ultramarine. The fine mica separated from the china clay in the washing is used for weighting coarse papers, paper boards, &c.

Ball clay, Potter's clay. The name given to certain sedimentary clays which fire to whitish or light-buff colour, and which possess high plasticity and tensile strength when in a moist condition. They are worked in Devonshire and Dorset, and in some parts of the United States, &c., and are chiefly used in the manufacture of white earthenware. They are generally finer in grain than china clay, contain more organic matter and other impurities, and are consequently more plastic in a moist state, and fire to a vitreous mass at a lower temperature. They usually also contain a higher percentage of silica than china clays.

Pipe clay. A rather loose term, which is applied to white clays which contain a relatively high percentage of silica, and which have been used without admixture for several hundred years for the making of tobacco pipes and also for common pottery. These clays are of various geological origins, and in some localities the

highly silicious clay found in pockets in lime-stone formations, and resulting from the decomposition of argillaceous limestones and chert rock, is used in this way. Ball clay is also used for the same purposes, and is sometimes consequently spoken of as pipe clay.

Plastic clay. This term has been specially applied to those beds of the Lower Tertiary or Eocene strata, which occur between the London clay and the chalk, and which may be recognised at Woolwich, Reading, Blackheath, Bognor, and in the neighbourhood of Paris, &c. This clay is mottled red or purple, and fires to a red colour. Some of our earliest pottery was manufactured from this clay, and it is still worked in Hampshire, in the Isle of Wight, and elsewhere.

Slate clay occurs in Devon, Cornwall, &c., differing considerably in different districts. It is massive, interspersed with mica, and of a greenish or greyish colour. It is sometimes hard and *slatey*, being readily cleavable into slabs, whilst in another form, the killas of the Cornish mines, it has an earthy fracture, is soft and frangible, and weathers to a more or less plastic clay. It is chiefly used for the manufacture of common bricks and tiles, and, when fairly free from lime, magnesia, and iron, for fire-bricks.

Common clay is the term often applied to the ordinary surface and drift clays which have been used for centuries for making common pottery and bricks.

Fireclays. As the name implies, these clays are of a very refractory nature, and although, strictly speaking, practically all the pure residual clays come under this head, the term 'fireclay' has been restricted in use to certain coal-measure shales which have a high fusion point, and which are used mainly for the manufacture of firebricks, gas retorts, glass pots, furnace linings, &c.

These fireclays usually underlie the coal seams, and are often worked in conjunction with the coal. Certain districts are particularly noted for the quality of their fireclays, and in England the Stourbridge coal-measure shales have long been considered of the highest quality, and fireclay-mines are extensively worked in the Stourbridge district. Good fireclays are also found and worked in the Lancashire and Yorkshire, Derbyshire, and Glasgow coal-fields. The fireclay shales are mostly greenish-grey in colour, compact, dense, and of varying degrees of hardness. On exposure to the weather they usually crumble down, and in time become converted into plastic clay. The weathering process may be greatly accelerated by grinding the shale, but this is only done when the clay is to be used for the more expensive fireclay goods. Only those coal-measure shales which contain small percentages of oxide of iron, lime, and magnesia, are sufficiently refractory to be used as fireclays, and although no definite fusion-point has been fixed, it seems advisable that no clay having a fusion-point lower than 1500° should be classed as a fireclay. In the manufacture of fireclay goods, the partially weathered or ground fire-clay is usually mixed with a certain proportion of 'ganister,' coarse sand, burnt clay, or other refractory material which produces in the fired ware a certain open texture, which enables it

better to withstand rapid changes of temperature. Certain silicious fireclays and other coal-measure clays are used in the manufacture of salt-glazed drain pipes, and also for making common culinary ware, buff-coloured tiles, terracotta, glazed bricks, &c.

Chemical analysis of clay. From 1–2 grams of finely powdered clay, dried at 120°, are weighed into a platinum crucible, and mixed with about six times its weight of a fusion mixture consisting of potassium and sodium carbonates in equimolecular proportions. The mixing is best performed by first stirring together the clay with about the same bulk of fusion mixture by means of a dry glass rod, and then adding more and more fusion mixture with repeated stirring, until the whole is thoroughly mixed. The glass rod should then be rubbed in a little fusion mixture, which is added to the mass in the crucible. The covered crucible is gradually heated over a Bunsen burner (a Teclu burner may be advantageously used) until the whole mass is in a state of tranquil fusion. The crucible is allowed to cool, and afterwards the bottom is raised just to dull redness, twice successively, in order to facilitate the removal of the mass from the crucible. After cooling, a few drops of distilled water are added, and the crucible very gently warmed until the mass detaches itself. The contents of the crucible are then washed into a large platinum dish (a porcelain dish may be used without seriously impairing the accuracy of the estimation), covered with water, and then warmed until the fused mass is completely softened. Hydrochloric acid is then added, a few drops at a time, until all effervescence ceases. The contents of the dish are evaporated on a water-bath, with constant stirring at the later stages, to ensure a fine powdery residue from which the last traces of hydrochloric acid are readily driven off. When cold, the contents of the dish are moistened with moderately strong hydrochloric acid, and allowed to stand for one hour ; water is then added, and the dish again heated on the water-bath The clear liquid is poured through a filter, and the residue in the basin, which consists of silicic acid, is washed repeatedly by hot water until it remains white when moistened with hydrochloric acid. The residue is then transferred to the filter, and washed with hot water until the filtrate no longer gives a precipitate with silver nitrate solution. The filter and contents are then placed in a platinum crucible and dried, and afterwards gradually heated, and finally ignited strongly until the paper is completely incinerated, and the weight constant. In order to ensure the complete separation of the silicic acid, it is necessary to evaporate the filtrate down to dryness, and treat exactly as before, and this process may be repeated again if very great accuracy is required. After filtering, the filter paper and residue are dried and added to the original silicic acid residue before ignition. The contents of the crucible are then weighed as silicon dioxide (SiO_2). If the clay contains titanic acid (as many clays do), this will accompany the silica. In order to determine the former, the contents of the crucible are covered with strong hydrofluoric acid, a few drops of sulphuric acid added, and the crucible warmed on the water-bath until all the silicon

fluoride and the sulphuric acid have been driven off. The residue is then weighed as titanic oxide (TiO₂), which should be identified by the violet-coloured bead with microcosmic salt.

The filtrate is made up to definite volume, and divided into two parts, one for the determination of the iron, and the other for the determination of the alumina, calcium, and magnesium. The iron is estimated as ferric oxide, and determined either by reduction with zinc and titration with potassium permanganate solution, or by the iodimetric method.

The other portion of the filtrate is heated on the water-bath, and ammonia added drop by drop, with repeated stirrings, until there is a *slight* excess of ammonia present. The liquid is then boiled for a moment and filtered. The precipitate is washed twice with hot water; washed back into a dish, and dissolved in hydrochloric acid; reprecipitated and filtered as before, and finally washed with hot water until the filtrate gives no precipitate with silver nitrate solution. The washing should be repeated immediately the previous washing has disappeared from the filter, and a jet of hot water should be directed into the precipitate so as to break it up as much as possible. The filter paper and contents are then dried, the residue removed into a platinum crucible, the paper separately incinerated, and then placed in the crucible, and the whole strongly ignited until the weight is constant. The contents are then weighed as alumina (Al₂O₃) and ferric oxide (Fe₂O₃), the amount of ferric oxide separately determined as above being deducted from the total, leaving alumina only (v. art. ALUMINIUM). The filtrate from the alumina and ferric oxide is concentrated, and ammonium oxalate solution added while hot. The precipitate is filtered off, thoroughly washed with hot water, dried, strongly heated, and weighed as CaO. The filtrate from the above is then concentrated, and the magnesium precipitated by sodium phosphate and ammonia. The precipitate is filtered off, dried, and ignited until the weight is constant. The ignited residue consists of Mg₂P₂O₇, and the weight must be multiplied by 0·3624 to give the amount of magnesia (MgO) contained.

Determination of the alkalis. The method introduced by Lawrence Smith (Amer. J. Sci. [2] 50, 269) is the most trustworthy, and is based on the decomposition of silicates by fusion with calcium carbonate. In practice, the dried and finely powdered clay is mixed with its own weight of ammonium chloride, and four times its weight of calcium carbonate. These latter materials must be as free as possible from alkali. The ammonium chloride used is prepared by subliming the commercial salt; and the calcium carbonate is prepared by dissolving the purest calcite obtainable in hydrochloric acid, and precipitating with ammonia and ammonium carbonate. The precipitation is carried out in a large porcelain dish, and, after settling, the clear liquid is poured off, and the precipitate washed by decantation until free from chlorides. A special platinum crucible is used for the fusion, about 8 cm. long, and 2 cm. diameter at the top, tapering to 1¼ cm. at the bottom. About 0·5 gram clay is weighed out, and mixed by rubbing in an agate mortar

with the same weight of ammonium chloride, and afterwards 3 grams of calcium carbonate are added, and the whole thoroughly mixed. The mixture is then transferred to the crucible, and the mortar is cleaned out with about 1 gram of calcium carbonate, which is added to the mixture in the crucible. The covered crucible is supported in an inclined position, and very gradually heated over a small Bunsen flame for about 15 minutes, until no more ammonia is given off, and then the temperature is raised until the lower three-fourths of the crucible is a dull-red, and this temperature is maintained for 1 hour. The crucible is cooled and the contents removed (by tapping the inverted crucible) into a porcelain or platinum dish. If the sintered mass sticks to the crucible, a little water should be added, and the crucible gently warmed until the mass detaches itself, and the whole can be washed into the dish. About 60 c.c. of distilled water are added, and the covered dish heated on a water-bath for 30 minutes, the water lost by evaporation being replaced, and the larger particles reduced by rubbing with an agate pestle. The clear liquid is decanted through a filter, and the residue washed by decantation four times, and then transferred to the filter and washed until the filtrate gives no precipitate with silver nitrate. The filtrate contains the alkalis as chlorides.

The calcium is precipitated by the addition of ammonia and ammonium carbonate to the filtrate, which is heated and filtered. The residue, which contains some alkali, is dissolved in hydrochloric acid, again precipitated by ammonia and ammonium carbonate, and filtered. The combined filtrates are then evaporated to dryness in a platinum dish, and the ammonium salts removed by careful heating over a moving flame. The residue is dissolved in water, and any traces of calcium left are precipitated by the addition of ammonia and ammonium oxalate. After standing 12 hours, the liquid is filtered off, evaporated to dryness in a weighed platinum dish, and gently heated. The alkali chlorides remaining in the dish are weighed, and the potassium determined by dissolving the chlorides in water and precipitating the potassium as potassium platino-chloride. The sodium is determined by difference.

Rational analysis of clay. To determine the relative amounts of clay substance, quartz, and undecomposed felspar, dry the clay, to constant weight, and weigh about 5 grams of the dried and finely powdered clay into a porcelain dish; add 50 c.c. of concentrated sulphuric acid and 100 c.c. of water, and then heat the mixture for 3 hours on a water-bath, and afterwards on a sand-bath, until the acid commences to fume. After cooling add water, and decant the clear liquid into a 2-litre beaker. To the residue in the dish add 10 c.c. of Lunge's solution (100 grams crystallised sodium carbonate, and 10 grams sodium hydroxide, dissolved in 1 litre of water), boil for 5 minutes, dilute with water, and decant into the beaker. Treat the residue in the dish similarly with concentrated hydrochloric acid, and repeat the treatment with Lunge's solution and hydrochloric acid, diluting with water after each treatment, and decanting the clear liquid into the beaker. Then wash the residue on to a filter with

dilute hydrochloric acid. Stir up the contents in the beaker, and allow to stand for an hour. Decant off the clear liquid, taking care to retain the residue in the beaker. Wash the residue into the dish, and repeat the treatment with Lunge's solution and acid as above, and pass through the filter. Wash with dilute hydrochloric acid, dry and ignite the filter paper and contents in a weighed platinum crucible. This residue is reckoned as felspar and quartz, and the loss suffered by the clay in this treatment as clay substance.

To determine the quartz and felspar, add about 5 c.c. of water, 4 drops of sulphuric acid, and 15 c.c. of hydrofluoric acid to the residue in the crucible, and heat the whole carefully on a sand-bath until nearly dry. Add more hydrofluoric acid, and again heat as before. After cooling, dissolve the mass in water, wash into a dish, and add ammonium chloride and ammonium hydrate to precipitate the hydroxides of aluminium and iron. Filter, wash with hot water, heat and weigh. This weight is multiplied by 5·451 to obtain its equivalent in potash felspar, and the difference between this and the weight of the original residue is taken as quartz.

Many ceramic chemists calculate the rational constitution of the clay from the ultimate analysis, taking the potash as derived entirely from undecomposed felspar (reckoned as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$), the alumina and iron as derived from felspar, and the clay substance (reckoned as $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and the silica as derived from the clay substance and quartz.

J. B.

CLAYITE. A name suggested by J. W. Mellor in 1909 for the non-crystalline variety of kaolinite $H_4Al_2Si_2O_9$, of which china-clay and most other clays are largely composed. The same name had been earlier used by W. J. Taylor, in 1859, for an uncertain alteration product (of tetrahedrite ?) composed of sulphur, arsenic, antimony, lead, and copper.

L. J. S.

CLAY IRONSTONE v. IRON, ORES OF.

CLAY SLATE v. SLATE.

CLAYTON CLOTH RED v. AZO- COLOURING MATTERS.

CLAYTON YELLOW v. PRIMULINE AND ITS DERIVATIVES.

CLEVEITE. A variety of uraninite, consisting of a uranate of uranyl, and oxides of lead and the rare earths. Usually obtained from Norway and Sweden. Hillebrand (Bull. U.S. Geol. Survey, 78, 43, 83) found the percentage of rare earths to be about 13, and that on heating with sulphuric acid, over 2 p c. of nitrogen was evolved. Ramsay (Chem. Soc. Trans. 1895, 1107) proved that the gas evolved was not nitrogen, but helium (q v.). Only half the helium is evolved by heat alone, and, moreover, in some cases the disengagement of the gas is accompanied by considerable evolution of heat (Proc. Roy. Soc. 1898, 64, 140). V. BROGGERITE and PITCHBLENDE.

CLEVE'S ACIDS. 1-Naphthylamine-6 and 7-Sulphonic Acids, v. NAPHTHALENE.

CLICHY WHITE. A white lead manufactured at Clichy, in France (v. White lead, art. LEAD.)

CLOTHBROWN, ·ORANGE, ·RED, ·SCARLET, v. AZO- COLOURING MATTERS.

CLOVE OIL v. OILS, ESSENTIAL.

CLOVER. The name by which several leguminous forage plants are known. The chief species are: white clover (*Trifolium repens*, Linn.); red clover (*T. pratense*, L.); alsike clover (*T. hybridum*, L.); crimson clover (*T. incarnatum*, L.); yellow suckling clover (*T. dubium*, Sibth.); mammoth red, or zigzag clover (*T. medium*, L.); hop clover, or hop trefoil (*T. procumbens*, L.). All the above belong to the true clovers, to the genus Trifolium. Also included as clover are: yellow clover, or trefoil (*Medicago lupulina*, L.); Bokhara clover, or melilot (*Melilotus alba*, Desn.); Japanese clover (*Lespedeza striata*, Hook et Arn.); and Soola clover, or sulla (*Hedysarum coronarium*, L.). The following table gives the average composition of various clovers at the time of flowering (Kellner):—

	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
T. repens	81·5	4 4	0·8	6·9	4·3	2·1
T. pratense	79·0	3·4	0·7	9·4	5 9	1·6
T. hybridum	81·8	2·8	0·7	7·0	6·2	1·5
T. incarnatum	81·5	2·8	0 7	7 0	6·1	1·9
T. procumbens	80·0	3·5	0 8	8 4	5·7	1·6
Melilotus alba	79·7	4·1	0·8	7·4	5·7	2·3

The following are analyses of hay from various clovers :—

	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
T. repens	9·7	15·7	2·9	39·3	24·1	8·3
T. pratense	16 5	13·5	2·9	37·1	24·0	6·0
T. hybridum	16·0	13·6	3·1	34·5	25·7	7·1
T. incarnatum	16·7	12 0	2·4	35·5	26·2	7·2
T. procumbens	16·0	15 4	3·4	33·2	24·5	7·5
Melilotus alba	15·7	16·7	2·8	27 9	30·3	8·0
Lespedeza striata	9·1	13·7	4·0	47·5	21·6	4·1

White or Dutch clover is a low, creeping perennial plant, valuable for grazing. Its growth in pastures is encouraged by phosphatic and potash manuring, but discouraged by nitrogenous manures In America, it is said that its blossoms salivate horses, and that consequently much clover in pastures is an objection where horses graze. White clover furnishes most excellent pasturage for bees, the honey which it yields being colourless and of high quality.

Red clover or broad clover is usually grown as a biennial, but will sometimes stand longer. It is often grown as a hay crop, or for cutting for green forage. It is the variety most susceptible to 'clover sickness,' and on many soils can only be grown safely once in 10 or 12 years.

A variety of red clover, *T. pratense* var. *perenne*, known as 'cow grass,' is not so prone to clover sickness, and lasts longer. It is, however, of slower growth, and usually yields but one crop per year of hay.

Alsike clover has whitish and pinkish flowers, and is a perennial; it is hardly susceptible to clover sickness.

Crimson clover, or 'trifolium,' is also a somewhat slow-growing crop, and is an annual.

Yellow suckling clover is a smaller plant than the other clovers, and is usually only grown in mixtures with rye-grass, &c. It is an annual.

Zigzag clover, known in America as mammoth red clover, ripens later than red clover, and is taller and ranker.

Bokhara clover, or large white clover, is a biennial, with small white flowers. This plant is remarkable for its strong odour, more pronounced when dried, of coumarin ; animals do not eat it readily until they become accustomed to it.

Soola clover is a perennial resembling red clover, but is richer in soluble carbohydrates (v. Scurti, Chem. Zentr. 1910, i. 1632).

As the table of analyses shows, clovers are remarkable for the large amounts of nitrogenous matter and of ash which they contain. Of the former, however, a considerable proportion is of a non-protein nature, particularly in the immature plants. In the case of red clover, for example, it has been found that about 40 p.c. of the total nitrogenous matter is present as amides in very young plants, and that the proportion diminishes with growth, until, when the plants are in full bloom, it is about 20 p.c., when fully ripe it sinks to about 12 p.c.

The ash of clovers is remarkable for its richness in lime and its poverty in silica (in which grasses and cereal straws are so rich).

The following are Wolff's analyses of various clover ashes :—

	K₂O	Na₂O	MgO	CaO	P₂O₅	SO₃	SiO₂	Cl
Red clover	34·5	1·6	12·2	34·0	9·9	3·0	2·7	3·7
White ,,	19·4	7·8	10·0	33·2	14·1	8·8	4·5	3·2
Alsike ,,	33·8	1·5	15·3	31·9	10·1	4·0	1·2	2·8

The very high ratio of lime to phosphorus pentoxide in the ash is noticeable.

Clover hay has proved very successful as a constituent of the rations of fattening oxen and sheep.

Out of about 200 feeding experiments with nearly 1000 cattle, conducted in Britain between 1833 and 1908, 17 included clover hay in the daily ration. The average daily increase in live weight per head of the whole was 1 803 lbs., while the consumption of total digestible matter per 1 lb. live weight gained averaged 9 lbs. In the 17 cases where clover hay formed a portion of the food, the figures are 2·1 lbs , and 7·47 lbs respectively (Ingle, Journ. High. and Agri. Soc. of Scotland, 1909).

With sheep, the results are equally significant. 2390 sheep fed in various ways, between 1844 and 1909, gave an average weekly increase per head of 2·06 lbs., and consumed an average of 7·43 lbs. total digestible matter per 1 lb. increase in live weight ; while 384 sheep receiving clover hay as part of their ration, gave an average weekly increase of 2·58 lbs. per head, and consumed only 6·20 lbs. of total digestible matter per 1 lb. increase in live weight (ibid. 1910).

H. I.

CLOVER FLOWERS. It has long been known that clover flowers dye a yellow colour on aluminium mordanted fabrics, and in the past they have been employed to a minor extent for dyeing purposes. Three varieties have been chemically examined, viz. those derived from the *Trifolium pratense*, the *T. incarnatum*, and the *T. repens*.

Trifolium pratense.—The flowers known as the 'common red clover,' according to Power and Salway (Chem. Soc. Trans. 1910, 97, 231), contain in addition to *isorhamnetin* (quercetin monomethyl ether) and a *glucoside of quercetin*, melting-point 235°, numerous other phenolic substances, which, judging by their chemical

properties, appear to be closely allied to the colouring matters of the flavone group. These are described below.

Pratol $C_{15}H_9O_2(OH)\cdot OCH_3$, colourless needles, melting-point 253°, readily soluble in hot aqueous sodium carbonate and sodium hydroxide with a pale yellow colouration, yields the *acetyl* compound, $C_{15}H_9O_2(OC_2H_3O)\cdot OCH_3$, and is probably a *hydroxymethoxyflavone.*

A *yellow compound*, $C_{16}H_{10}O_7$, thin yellow plates, melting-point about 280°, is soluble in alkalis with a yellow colour, and its solution in sulphuric acid exhibits a brilliant green fluorescence. It contains a methoxy group and gives an acetyl compound, $C_{16}H_6O_7(C_2H_3O)_4$, melting-point 145°-147°.

Pratensol, $C_{17}H_9O_2(OH)_3$, is very readily soluble in alcohol, dissolves in alkali carbonates yielding yellow solutions, and its alcoholic solution gives with ferric chloride a greenish-black colouration. *Triacetylpratensol* $C_{17}H_9O_5$ $(C_2H_3O)_3$, colourless slender needles, melts at 189°.

A *phenolic substance*, $C_{15}H_7O_2(OH)_3$, colourless needles, melting-point 225°, is soluble in alkali hydroxides, and gives with alcoholic ferric chloride a dark green colouration. The *acetyl* derivative, silky needles, has melting-point 209°.

The glucoside *trifolin* $C_{22}H_{22}O_{11},H_2O$, pale yellow needles, melts and decomposes at about 260°. It is soluble in alkalis with an intense yellow colouration, and dissolves in sulphuric acid, forming a yellow solution, which rapidly develops a brilliant green fluorescence. When hydrolysed it yields rhamnose and *trifolitin* $C_{16}H_{10}O_6$, melting-point about 275°, readily soluble in alcohol,

$$C_{22}H_{22}O_{11} = C_{16}H_{10}O_6 + C_6H_{12}O_5$$
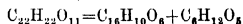
Alkalis dissolve trifolitin with an intense yellow colour, alcoholic ferric chloride gives a dark green colouration, and alcoholic lead acetate an orange-yellow lead salt. It contains no methoxy group, and is unaltered when heated for several hours with 30 p.c. aqueous potassium hydroxide. It does not appear to belong to the flavone group, and differs from the flavone compounds by the fact that it does not give an oxonium salt with sulphuric acid, and only with difficulty a potassium compound by means of alcoholic potassium acetate. It may possibly consist of a tetrahydroxyphenylnaphthoquinone. The acetyl compound when rapidly heated melted at 116°, re-solidified at a higher temperature, and finally melted at 182°.[1]

The glucoside *isotrifolin* $C_{22}H_{22}O_{11}$, isomeric with trifolin, consists of pale yellow needles, melting-point about 250°, and when hydrolysed yields similarly to the latter trifolitin, $C_{16}H_{10}O_6$, melting-point 275°. Though in general behaviour it is very similar to *trifolin*, it is much more soluble in alcohol, and does not appear to be identical with this glucoside.

In addition to these compounds the flowers contain *salicylic acid, coumaric acid, myricyl alcohol* $C_{31}H_{63}OH$, *heptacosane* $C_{27}H_{56}$, *hentriacontane* $C_{31}H_{64}$, *sitosterol* $C_{27}H_{46}O$; *trifolianol* $C_{21}H_{34}O_2(OH)_2$, *palmitic, stearic, linolic, oleic, linolenic,* and *isolinolenic* acids.

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[1] Both in its melting-point and that of its acetyl derivative there is a marked resemblance between trifolitin and kaempferol.

Trifolium incarnatum.—A considerable difference is exhibited between the constituents of the ' carnation or crimson clover flowers ' and those of the *T. pratense* or ' common red clover.'

According to Rogerson (Chem. Soc. Trans. 1910, 97, 1006) these flowers contain *pratol* $C_{15}H_8O_2(OH)(OCH_3)$, free *quercetin*, and a *glucoside of quercetin* $C_{21}H_{20}O_{12},3H_2O$, to which the name *incarnatrin* is applied. This latter crystallises in yellow prismatic needles, melting-point 242°–245°, dissolves in sulphuric acid with formation of a green fluorescent solution, and when hydrolysed yields quercetin and glucose according to the equation

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_8$$
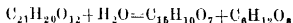
Incarnatrin is not identical with the quercimeritrin of Perkin (Chem. Soc. Trans. 1909, 95, 2181).

In addition to these substances the flowers yield *furfuraldehyde, benzoic* and *salicylic acids,* a trace of *p-coumaric acid, incarnatyl alcohol* $C_{34}H_{69}OH$, *hentriacontane* $C_{31}H_{64}$, a *phytosterol* $C_{27}H_{46}O$, and *palmitic, stearic, oleic, linolenic,* and *isolinolenic acids*

Trifolium repens.—The flowers of the white clover, *T. repens,* according to Perkin and Phipps (Chem. Soc. Trans 1904, 85, 58), owe their tinctorial property to quercetin which is present as glucoside.   A. G. P.

CLOVES. The cultivation of cloves forms the most important industry of Zanzibar and of the island of Pemba. In 1913–14 the total crop was 25,431,735 lbs of which 20,692,771 lbs came from Pemba, where about two-thirds of the total area, or about 35,000 to 40,000 acres, are under clove cultivation The crop is, however, very uncertain, the amount in some years not being above one sixth of the above yield Large trees may furnish from 60 to 70 lbs. of dry cloves, although the average yield is only about $3\frac{1}{2}$ to 4 lbs per tree per annum. The cloves are picked by hand and dried in the sun. The value of cloves depends upon the amount of essential oil present, the quantity of which may vary from about 6 to 20 p c. Of this oil about 84 to 90 p.c. consists of eugenol. (*V.* Clove Oil in art. OILS, ESSENTIAL.)

COAL *v.* FUEL.

COAL GAS *v.* GAS, COAL.

COBALT. Sym. Co. At. wt. 58·97.

Cobalt usually occurs combined with arsenic or sulphur, and almost invariably associated with nickel and other metals. Free cobalt occurs only in meteorites.

The most plentiful and important ore of cobalt is *smaltine* or *tin white cobalt,* consisting of arsenide of cobalt, nickel, and iron. It occurs abundantly at Schneeberg and many other localities where bismuth is found (*v.* BISMUTH), in Bohemia, at Balmoral near Pretoria, near Sudbury in Ontario, very pure at Tunaberg in Sweden, and free from nickel in Colorado As triarsenide, it forms *skutterudite* CoAs₃ Sulphar-senide of cobalt occurs as *cobalt glance, grey cobalt,* or *cobaltine,* abundantly at Vena (Sweden) and in Norway ; in smaller quantities in Silesia and Cornwall. As hydrated arsenate it forms *cobalt bloom* or *erythrite* $Co_3As_2O_8,Aq.$, found frequently as a peach-coloured incrustation on other arsenical ores, being produced by their decomposition. As sulphide, cobalt occurs

in small quantities in *cobalt pyrites* and in *linnaeite.*

Black earthy cobalt is a hydrated oxide of cobalt and manganese. It is essentially a variety of *wad* (hydrated manganese oxide), containing sometimes as much as 40 p.c. of cobalt. Surface deposits containing oxides and sulphides of cobalt and of nickel occur at New Caledonia, with veins of chrome ore and nickel and magnesium silicates ; it is smelted on the spot and exported as a regulus to England. Cobalt occurs in small quantities in many other minerals ; in pyrites and in certain iron ores ; as oxide in black oxide of manganese ; as arsenide in mispickel, sometimes to the extent of 10 p.c. ; in selenide of lead, and in cerite, and in some peats and coals.

At the present time the most important source of cobalt, whence almost the whole of the cobalt of commerce is obtained, is the district surrounding Cobalt city, near the shores of Lake Temiskaming in North Ontario. Here very rich silver ores are found, containing frequently 2000 oz silver per ton, and sometimes as much as 60 p.c. These ores also contain a high percentage of cobalt and nickel, chiefly as arsenides, and, after extraction of the silver, are sent to nickel and cobalt refiners.

Extraction.—The methods adopted by manufacturers for the extraction of cobalt from the ores vary with the nature of the ores. The ores are first concentrated by fusing with a suitable flux, whereby silicious matter and a portion of the iron are removed. In the case of the Ontario ores, the speiss consists chiefly of arsenides of cobalt, nickel, iron, and copper. The speiss is then calcined, the iron is oxidised to ferric oxide, part of the arsenic is removed, a little less being left than is required to combine with the iron. The mass is then dissolved in hydrochloric acid, and bleaching powder and lime are added, whereby the iron is precipitated as arsenate and hydroxide. The liquid is then treated with sulphuretted hydrogen to precipitate copper and other heavy metals, excess of the gas evaporated off, and the cobalt precipitated as oxide by the addition of bleaching powder. The nickel in the solution is subsequently precipitated by potash or lime.

In the case of New Caledonian ores, consisting chiefly of sulphides, the treatment of the concentrated ore is somewhat different. The *matt,* consisting chiefly of sulphides, is carefully calcined at a moderate temperature, and converted into sulphates. These are dissolved in water, and the iron precipitated by careful addition of the requisite quantity of sodium carbonate. The copper and heavy metals are separated by sulphuretted hydrogen, and after boiling off the excess, the cobalt is precipitated by sodium hypochlorite (bleaching powder cannot be used, owing to the sulphates in the solution), and the nickel in the remaining liquid precipitated by sodium carbonate.

In Herrenschmidt's process for the treatment of New Caledonian ores, these are treated with a solution of ferrous sulphate, when cobalt, nickel, and manganese pass into solution, and iron remains in the residue. Copper is first separated, and then the cobalt, nickel, and manganese precipitated by sodium sulphide. The manganese is extracted by ferric chloride, the nickel and cobalt sulphides roasted to

sulphates, and converted into chlorides by calcium chloride. A part of the solution is treated with lime water, and the suspended precipitate oxidised by chlorine and added to the other portion, whereby the cobalt is precipitated and nickel chloride remains in solution.

Until of late years the only market for cobalt compounds was in the ceramic industry, in which it was employed for whitening the body of china and in the production of blue colour. It is employed in the enamelling trade, the manufacture of blue-coloured signs, the colouring of glass and in the manufacture of pigments and as driers for paints.

Metallic cobalt is not at present used to any extent in the arts, though its utility is becoming more fully recognised, especially in electroplating and in high-speed steels and in 'stellite,' an alloy of cobalt, chromium and tungsten. Commercially it is always prepared by heating the oxide with charcoal; it then contains small quantities of carbon. Pure cobalt is prepared by heating cobalt oxalate $Co(CO_2)_2$, when the carbon and oxygen pass off as carbonic anhydride, leaving the pure metal as a powder. A button of the fused metal may be obtained by fusion of the oxalate alone, or of the oxide mixed with charcoal under a layer of powdered glass containing no lead or other reducible metal; the fusion is preferably performed in a lime crucible at the highest temperature of a furnace. Pure cobalt may also be prepared by electro-deposition with platinum electrodes (Winkler, Zeitsch. anorg. Chem. 8, 1). Cobalt is also produced as a grey metallic powder by igniting the oxide at a red heat in a current of hydrogen. If too low a temperature has been used, the metal produced is *pyrophoric*, igniting and becoming reoxidised in contact with the air.

Carbon monoxide rapidly reduces cobalt oxide at all temperatures above 600°, the reduction being complete at 900°. With charcoal complete reduction takes place at 900°, the final product containing about 2 p.c of carbon. Reduction with aluminium by the thermit process gives a metal containing about 0·1 p.c. of aluminium or even less (Kalmus, J. Ind. Eng. Chem. 1914, 6, 107).

Properties.—Cobalt is a brilliant silver-white metal, with a slight bluish cast. It is the most magnetic metal after iron, and retains its magnetism at high temperatures; above 1115° it passes into a non-magnetic variety.

Pure cobalt is harder and more tenacious than iron, its breaking weight being about 50 kilos. per sq. millimetre. Valenciennes states that cobalt, after fusion and annealing, may be rolled into spiral bands like good iron (Compt. rend. 70, 607). Cobalt melts at 1530° (Copaux), 1490° (Henning), 1478° (Kalmus & Harper), and boils at 2415°/30 mm. Its sp.gr. is 8·8, and hardness, 5·5. Its specific heat (20°-100°) is 0·104; specific resistance, 5·5; and the temperature coefficient of resistance, 0·0055. According to Kalmus & Harper (J. Ind. Eng. Chem. 1915, 7, 6), pure cobalt prepared by reduction of cobalt oxide has D_4^{17} 8·7918 (unannealed), $D_4^{14·5}$ 8·8105 (annealed), $D_4^{16·5}$ 8·9253 (swaged); m.p. 1478±1·1°; tensile strength, cast and unannealed, 34,400 lb.

per sq. in.; annealed 36,980 lb. per sq. in.; and rolled, more than 100,000 lb. per sq. in.; compressive strength, cast and unannealed, 122,000 lb. per sq. in., annealed, 117,200 lb. per sq. in.; electrical resistance 89·64 ohms per cm.³; specific heat, from 0° to 890° 0·1058 $+0·0000457t+0·000000066t^2$. The hardness of cast cobalt is considerably greater than that of either iron or nickel, being approximately 124·0 (load 3500 lb.). The presence of from 0·06 to 0·3 p.c. of carbon in the metal increases the tensile and compressive strength, and the electrical resistance, but has little effect on the hardness. Pure cobalt may be machined in a lathe as readily as pure iron or nickel, but it is somewhat brittle; cobalt containing a small quantity of carbon machines like mild steel, and whilst pure cast cobalt cannot be rolled or swaged without developing cracks, cobalt containing carbon may be rolled or swaged down from cast bars to any extent provided that the metal is worked at a red heat (Chem. Soc. Abst. 1915, ii. 99). It is slowly soluble in hydrochloric and sulphuric acids, with evolution of hydrogen, quickly soluble in nitric acid; it is not attacked by hot or cold alkali, but if used, as anode in the electrolysis of alkaline electrolytes, passes into a colloidal solution of cobaltous oxide. It exhibits also the *passive* state, similar to that of iron and other metals, but the tendency to do so is slight. Cobalt occludes from 60 to 150 times its own volume of hydrogen, the amount varying with the mechanical condition of the metal. The powdered metal combines, when heated, with chlorine, bromine, and iodine. It decomposes steam at a red heat, and, if finely divided, ignites when heated in oxides of nitrogen, and in a current of ammonia gas at 500° forms a nitride Co_2N_2. When finely divided cobalt is heated to 150°-200° in carbon monoxide at 100 atmos. pressure, orange-red crystals of *cobalt carbonyl* $Co(CO)_4$ are formed, melting at 51°, soluble in alcohol or ether, but insoluble in water, and decomposing above 52°, yielding $Co(CO)_3$ which further decomposes (Mond, Chem. Soc. Trans. 1910, 798) (v. Cobalt Carbonyls).

Cobalt may be deposited as a fine lustrous coating on metals by the electrolysis of a neutral solution of the double sulphate of cobalt and ammonium, using a current of about 6 amperes per sq. foot of cathode surface, and an anode of cobalt (A. Gaiffe, Compt. rend. 1878). The presence of ammonium chloride appears to hinder, whilst ammonium sulphate assists, the deposition. The deposit of cobalt is harder, more tenacious, and of greater beauty than that of nickel (Troost).

(For the properties of cobalt containing other metals, v. *Alloys of cobalt.*)

Detection.—All ores and compounds of cobalt impart a blue colour to a bead of borax on fusion; if present in too great excess, the bead appears black. Heated on charcoal with reducing flux, all substances containing cobalt produce metallic particles which are attracted by a magnet (distinction from all other bodies except iron and nickel).

Salts of cobalt, when *strongly* heated with alumina before the blowpipe, give a fine blue colour (Thenard's blue). Sulphuretted hydrogen produces no precipitate in an acid solution, but gives a black precipitate of sulphide in

alkaline solutions, the precipitated sulphide being insoluble in dilute acids. In a solution containing free acetic acid, potassium nitrite produces a yellow precipitate of potassium cobaltinitrite $K_3Co(NO_2)_6$; the whole of the cobalt being thus precipitated on standing in a warm place for some time. If a mineral acid is present, it should first be neutralised by potassium hydroxide.

Potassium thiocyanate with cobalt salts gives a red colouration, and, on the addition of alcohol and ether, forms a deep *blue* ethereal layer.

Cobalt is also precipitated as a red precipitate by the addition of a solution of nitroso-β-naphthol to its alcoholic or acid solutions. As nickel is not thus precipitated, this forms a useful means of separation of the two metals, the sulphides being dissolved in *aqua regia*, evaporated to dryness, taken up with a little water and hydrochloric acid, and precipitated as above.

Estimation —Ores containing cobalt are usually very complex; they almost invariably contain nickel and many other metals from which the separation is difficult. The following scheme will serve for the estimation of both cobalt and nickel in any mineral, though in the case of certain ores it may be somewhat simplified.

From 2 to 7 grams of the finely ground ore are roasted in a porcelain crucible in a muffle. The residue is boiled with hydrochloric acid containing a little nitric acid until the metallic oxides are dissolved; the solution is diluted, nearly neutralised with ammonia, and boiled with sodium acetate solution, whereby the iron and aluminium are precipitated as acetates containing the greater part of the arsenic (as arsenate of iron) and a little nickel and cobalt. The solution is filtered, and the precipitate redissolved in hydrochloric acid and reprecipitated as before, the precipitate being this time free from nickel and cobalt. The two filtrates are mixed, just neutralised with ammonia, and treated with sulphuretted hydrogen gas; cobalt, nickel, zinc, copper, bismuth, &c , are thus precipitated as sulphides, leaving the manganese and the alkaline and earthy metals in solution. The precipitate is filtered, washed, dried, and roasted, the oxides so produced dissolved in hydrochloric acid, and treated with sulphuretted hydrogen; the copper, bismuth, lead, &c., are thus precipitated and filtered off.

The solution is boiled till free from sulphuretted hydrogen, and the two metals co-precipitated by the addition of potash to the boiling solution; the precipitate is filtered and washed, nearly dried, and separated as far as possible from the filter. The precipitate is digested in a dish with dilute hydrocyanic acid, then with potash solution, and again with hydrocyanic acid, and warmed until no further solution occurs. A minute quantity of residue is left, consisting of paracyanogen and a small quantity of the oxides of nickel and cobalt; it is added to that still remaining on the filter paper, and the whole washed, dried, heated, and weighed.

The solution containing the two metals is boiled to expel the excess of acid, and consists of cobalticyanide of potash and double cyanide of nickel and potash. Precipitated yellow mercuric oxide is added, and the solution boiled for some time. The nickel is thus precipitated, partly as cyanide and partly as sesquioxide. It

is filtered, washed, dried, heated, and weighed as nickel protoxide NiO. The filtrate is nearly neutralised with nitric acid, and a neutral solution of mercurous nitrate added in excess. The cobalt is thus precipitated as mercury cobalticyanide, which is washed, dried, and heated in an open crucible until of constant weight. The product consists of Co_3O_4.

From the proportions of cobalt and nickel thus found, the amount of each in the residue on the filter paper, &c., which has been weighed may be calculated, and added to the amounts directly determined.

In other methods, the copper, &c., are first precipitated by sulphuretted hydrogen, iron by ammonia, and the nickel and cobalt precipitated as sulphides. The sulphides are redissolved, and in (1) the total nickel and cobalt estimated by electro-deposition; in (2) the cobalt is first precipitated and the nickel alone determined.

The cobalt in the above solution may also be determined by precipitation as potassium cobaltinitrite, dissolving the precipitate in warm dilute sulphuric acid, evaporating nearly to dryness, and electrolysing after addition of ammonium oxalate and excess of ammonium carbonate (Copaux, Bull. Soc. chim. iii. 29, 301)

The solution containing the sulphides of nickel and cobalt may also be estimated after freeing from excess of acid by boiling with barium carbonate, and adding excess of bromine water After 10 minutes the cobalt is completely separated as sesquioxide (Taylor, Proc. Man Phil. Soc. 46, 1).

Various volumetric methods have been suggested, but none appears to be perfectly satisfactory.

Alloys of Cobalt. Cobalt unites with incandescence on fusion with *antimony* or *arsenic*, forming brittle iron-grey alloys.

With *arsenic* the freezing-point curve indicates the existence of compounds, Co_5As_2; Co_2As; and Co_3As_2. *Smaltine* $CoAs_2$ forms tin-white octahedra; and *skutterudite* $CoAs_3$ occurs as greyish-white octahedra. The arsenides are attacked by oxidising agents, and all containing over 38 p.c. arsenic are non-magnetic.

Antimony and cobalt are completely miscible in the liquid state. Three classes of alloys exist : magnetic alloys with less than 67 p.c. antimony; alloys of from 67 to 80·27 p.c., which on heating form CoSb; and alloys above 80·27 p.c., which by acids yield a compound, $CoSb_2$, as a grey crystalline powder (Ducelliez, Compt. rend. 147, 1048).

Cobalt has a marked effect on the electrical properties of *copper*; 3·5 p.c. gives an alloy with a temperature coefficient of the resistance of only 0·00077. Two series of mixed crystals appear to exist, 0–10 p.c., and 95–100 p.c. copper, and alloys within these limits consist of conglomerates of the two sets of mixed crystals. Some of the alloys are very ductile. As in many of the cobalt alloys at high temperatures, the cobalt is present as a non-magnetic form (*β*), which changes to the magnetic (*a*) form on cooling. Alloys containing 99 p.c. of copper are stated to be magnetic (Sahmen, Zeitsch. anorg. Chem. 57, 1).

Tin and cobalt are perfectly miscible as liquids, and, according to Ducelliez (Compt. rend. 148, 502), all alloys are mixtures of CoSn

and Co_3Sn_4 with one another, or with either of the components. Below 57·6 p.c. tin, the alloys are magnetic and brittle ; above 66·8 p.c. tin, the alloys are less brittle and non-magnetic ; all are much harder than either component. A compound Co_4Sn of m.p. 1151° has also been described.

With *gold* a brittle alloy is produced, that containing 1 part gold and 17 parts cobalt is dark-yellow and very brittle ; all the alloys are magnetic. With *platinum* a fusible alloy is produced ; and a silver-white magnetic amalgam with *mercury* is used in dentistry.

Alloys with *aluminium* containing less than 68·5 p.c. cobalt are non-magnetic, the freezing-point curve indicates a compound CoAl Cobalt and nickel do not appear to form a compound ; the freezing-point curve is almost straight, the composition of the solid being almost identical with that of the liquid in all cases.

Addition of *iron* has no appreciable effect on the melting-point of cobalt, the curve being almost horizontal to 5 p.c. cobalt, the crystals having the same composition as the fused mass. Two series of non-magnetic, which transform into four series of magnetic crystals, appear to exist (Tammann, Zeitsch. anorg. Chem. 45, 205). Steels containing up to 60 p.c. cobalt show perlitic structure, and the mechanical properties are only slightly affected by the cobalt.

Lead, silver, or *bismuth* are only partially miscible with cobalt when molten, and no definite alloys appear to be formed.

With *silicon* in the electric furnace, steel-grey metallic-looking silicides are formed, Co_2Si and $CoSi_2$. Both are stable and hard, and attacked by hydrofluoric acid and *aqua regia*. A very hard magnetic *boride* is prepared in a similar manner ; and by the action of phosphorus on cobalt chloride at a low red heat a hard brittle *phosphide,* Co_2P_3, not affected by heat or acids, is produced.

It is possible to combine cobalt or nickel with manganese with the production of valuable alloys. For this purpose commercial manganese or ferro-manganese may be used, the presence of iron not being injurious. From 2 to 5 p.c. of the manganese is added in small portions to the molten metal ; much gas is evolved after each addition, and the metal is poured into moulds when tranquil (*v.* Huntington, J. Soc. Chem. Ind. 1882, 258).

It is stated that when in the molten condition cobalt and nickel take up both carbon and oxygen, but evolve the greater part of the latter substance on cooling, leaving a porous metal containing carbon. A method has been patented whereby this carbon is said to be eliminated. The porous cubes of metal are immersed in a 4 p.c. solution of alkaline manganate or permanganate, dried and melted in a crucible at a high temperature. The carbon is said to be thus oxidised and removed, and the metal takes up a small quantity of oxygen. As soon as the metal flows easily, a little black flux and charcoal, or a small quantity of aluminium, or the calcium zinc produced in Caron's process, is added, and the oxygen thus removed (Dingl. poly. J. 1884, 254–315).

Oxide of cobalt is used for the preparation of the salts of cobalt and of smalt, and by enamellers and porcelain manufacturers for the production of the finest blue glaze and colour on porcelain, glass, and other vitrifiable substances. The presence of $\frac{1}{50000}$ of this substance imparts a bluish tinge to clear glass.

The presence of other oxides has an injurious effect on the colour produced by this substance (*v. Smalt*) ; it is therefore necessary, for the more delicate work, to ensure its complete freedom from such impurities.

When heated strongly with magnesia, it produces a pink mass ; with alumina, a fine blue (Thenard's blue) ; and with zinc oxide, a green (Rinmann's green). *Zaffre* consists of a very impure oxide of cobalt, produced by roasting the ore. It is usually mixed with 2 or 3 parts of fine sand or ground quartz, and is used for the same purpose as smalt for the coarser work.

Cobalt blue, Cobalt ultramarine, Thenard's blue, Azure blue. The composition of this pigment varies considerably, according to the method of manufacture. It consists sometimes of the oxides of cobalt and aluminium ; at other times it contains phosphate or arsenate of cobalt.

It may be prepared by first precipitating a solution of a cobalt salt, usually the nitrate, free from iron and nickel, with potassium or sodium phosphate, or with sodium arsenate. The gelatinous violet precipitate is thoroughly washed and well mixed with 3–5 volumes of freshly precipitated, well-washed alumina (when cobalt arsenate is employed, a larger proportion of alumina may be added), precipitated from a solution of alum free from iron by the addition of sodium carbonate. The mixture is dried until it becomes brittle, and calcined at a cherry-red heat for 30 minutes in a well-covered clay crucible. When the desired blue colour has been developed, the mass is ground with water and dried. In order to prevent the possibility of entrance of reducing gases, which much injure the value of the product, Regnault recommended the addition of a little mercuric oxide before the ignition. This becomes decomposed and evolves oxygen, which effectually prevents reduction, while the mercury escapes as vapour (Regnault, Cours Elém. de Chimie, 3, 150).

A similar but less fine colour is produced by the simultaneous precipitation of the oxides of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate and alum ; the mixed precipitate is washed and treated as above.

According to the process recommended by Binder (Technologiste, 5, 55), the oxide of cobalt is precipitated by the addition of the requisite quantity of ammonia to a solution of pure cobalt chloride. The washed precipitate is mixed with alumina as before, dried, and calcined at a red heat in a clay crucible for two hours.

According to Hedvall the fusion of cobaltous oxide and alumina is best made in presence of potassium chloride as a flux. When the cobalt oxide is in excess the resulting product can be obtained pure by treatment with water to remove the flux and with hydrochloric acid to remove the excess of cobalt oxide. At 1100° the blue aluminate $CoO·Al_2O_3$ is formed ; at temperatures above 1100° a *green aluminate* $4CoO,3Al_2O_3$ is produced. McEachern has pointed out that alumina and cobalt oxide alone do not produce a satisfactory colour, but that additions of sodium or magnesium salts greatly improve it. Wagner and Vanino found

that cobalt sulphate could be used instead of phosphate, and that the alumina was most suitably introduced as ammonium-alum. To 25 pts. of alum were added 2·5 to 5 pts. cobalt sulphate, 0·3 pt. magnesium or zinc sulphate; the mixture is melted in its water of crystallisation and constantly stirred until dry, when it is heated to the required temperature (Vanino, Chem. Zeit. 1911, 35, 497).

Thenard's blue is of a fine ultramarine colour; the presence of excess of cobalt imparts a somewhat greenish tinge. It has, however, the disadvantage of appearing violet by gaslight. It is one of the most permanent blue pigments, being unaltered by acids or alkalis, and is largely used as an oil and water colour, but works better as water colour It is non-poisonous, and has the advantage of miscibility with other pigments without alteration.

Cœruleum, *Cœline, Bleu céleste,* is a corresponding colour containing oxide of tin and usually calcium sulphate. Its general composition is said to be oxide of tin, 49·66; oxide of cobalt, 18·66; calcium sulphate and silica, 31·68; and a pigment of this nature is obtained by precipitating a solution of cobalt nitrate with sodium stannate, and heating the precipitate as above.

It is a fine light-blue pigment of slightly greenish tinge, of greater density than Thenard's blue, and retains its colour in artificial light

New blue. A blue pigment of shade varying from a pale-greenish blue to a deep-turquoise blue, largely used for enamels, consists of aluminates of cobalt and chromium produced by the action of alum on carbonates and hydroxides of cobalt and chromium.

Cobalt green, *Rinmann's green.* The constitution of this pigment corresponds with that of Thenard's blue, with the substitution of zinc oxide for alumina.

It may be prepared by mixing a solution of pure cobalt sulphate (or nitrate) into a paste with zinc oxide, and heating in a muffle furnace for 3 or 4 hours, until the desired colour is obtained. Pigments of a more uniform nature are produced by the precipitation of a mixture of solutions of zinc and cobalt salts, by means of sodium carbonate, phosphate, or arsenate, drying and heating the precipitate. The phosphate is said to give a purer and brighter green than the carbonate.

R. Wagner (Technologiste, 18, 409) gives the composition of fine green pigments as varying from 71·68 p.c. zinc oxide and 11·62 p.c. cobalt oxide, to 88 04 p.c. zinc oxide and 11·52 p.c. cobalt oxide, the quantity of phosphoric oxide also varying greatly.

According to Hedvall (Arkw. Kem. Min. Geol. 1913, 5, No 6, 1), Rinmann's green is not a definite substance, but rather a series of solid solutions of its component oxides in isodimorphic crystals.

Rinmann's green is a fine permanent pigment; its colour varies through many shades, according to the proportion of zinc present, the darker greens containing less of that substance It is non-poisonous and unacted upon by dilute acids or alkalis, but is attacked by ammonia. It has also the advantage of not affecting or being unaffected by other pigments. Rinmann's green, on account of its high price, and

the number of other permanent greens, finds little use as a pigment. Another permanent green pigment used in porcelain painting is said to be prepared by the calcination of a dried mixture of the following proportions of the freshly precipitated substances; 20 cobalt carbonate, 40 alumina, 20 chromium oxide.

Cobalt bronze is a phosphate of cobalt and ammonia, of a violet colour, with a bronze-like metallic lustre

Cobalt silicates. A cobalt silicate is produced by the addition of sodium silicate (soluble glass) to a cobalt salt. It produces a blue pigment well suited for painting on glass and porcelain.

Smalt. *Bleu d'azur, Bleu de Saxe.* This important substance consists of a silicate of cobalt and potash

In the preparation of smalt in Saxony, smaltine is principally used In Norway and Sweden the principal ore is cobaltine The general process is identical for both ores.

The selected ore is powdered, freed from the lighter earthy impurities by washing, and placed, in charges of about 3 cwt , in a layer of 5 or 6 inches thick on the bed of a reverberatory furnace or in a muffle It is then roasted, and the sulphur and arsenic expelled as oxides, the latter being condensed in chambers through which the fumes are passed The roasting must be discontinued when only sufficient arsenic is left to combine with the less oxidisable metals, especially copper and nickel, while the greater part of the cobalt is converted into oxide. In order to ascertain whether the roasting has proceeded sufficiently, a small portion is occasionally tested and the process stopped when the finest tinted glass is produced. The material is then ready for fusion for 'smalt.'

The fluxes used consist of powdered quartz and potassium carbonate They must be of great purity, as the presence of lime and many other substances impairs the beauty of the colour. The quartz is first heated to redness, plunged into water, and, thus disintegrated, is powdered in a mill It is then suspended in water and allowed to subside for a short time, and the liquid, which contains most of the iron and other impurities still suspended, is poured off; this operation is repeated until a pure quartz powder is obtained.

The proportions of the ingredients used vary extremely according to the richness of the ore and the colour required. The potassium carbonate used generally amounts to about one-third of the weight of ore and quartz together. White arsenic is usually added to oxidise any ferrous-salt, and thus prevent the injurious effect of that substance on the smalt, and to otherwise heighten the colour of the product. The exact amount of each of these substances is found by a test fusion and comparison with a smalt of the required colour.

The smalt furnace is similar to a glass oven; it usually contains eight crucibles. The pots are of very refractory clay, free from lime, and capable of holding ¾ cwt. When charged, they are strongly heated, and the mass fuses in about 8 hours; it is frequently stirred to render it homogeneous, and to break the crust which forms on the surface. At a white heat combination occurs, the quartz and potash react with the production of fusible potassium

silicate, which dissolves the cobalt oxide, forming the blue 'smalt,' while the mixed arsenides of nickel, copper, and iron, with the small quantity of cobalt arsenide which is always present, fuse and form a brittle metallic-looking *speiss* beneath the smalt. This usually contains about 3 p.c. of cobalt and a considerable quantity of nickel, and is used for the preparation of the latter substance and of cobalt oxide. The mass is left at a white heat for some time without stirring, to allow the speiss to settle, and is ladled out with long-handled iron ladles into vessels of cold water. It is thus rendered granular, brittle, and easy to pulverise. When nearing the bottom of the crucible, the ladle contains both speiss and smalt; the former, being much more fusible, is poured first from the ladle, from beneath the smalt, into a niche in the side of the furnace, whence the dense fumes of arsenic, &c., which it evolves pass up the chimney.

The blue glass is next powdered with granite stampers, or ground between granite millstones under water, and the product passed through a series of depositing vats In the first vat it remains for a short time only, thence it passes to a second for a somewhat longer time, to a third for about 15 minutes, to a fourth and fifth for a corresponding period, and finally to a sixth vat, where it is allowed to deposit completely. The deposit in the first vat is returned to the mill and re ground, that in the second and third is the best marketable smalt, whilst in the fourth and fifth vats a lighter-coloured deposit, sold under the name *eschel*, is produced. The deposit in the last vat is not marketable, and is usually resmelted.

The marketable deposits are again washed, deposited, dried, powdered, and sifted. About three-fifths of the glass taken from the pots is thus available The presence of other oxides than those of cobalt and potash, even in small quantities, exerts a powerful influence on the colour of the smalt. Baryta produces an indigo tinge; sodium, calcium, and magnesium produce a reddish shade; iron, a blackish green, very prejudicial to the brighter-coloured smalts; manganese violet, nickel violet, but less intense; copper, zinc, bismuth, and antimony, dull shades.

The composition of smalt varies considerably; the silica is usually from 56–70 p c.; potash, 12–22 p.c.; and cobalt, 6–16 p.c. The following analyses by Ludwig (J. pr. Chem. 1850, 51, 129) are typical :—

	Norwegian deep-coloured smalt	German deep-coloured	German pale coarse
Silica . .	70·86	66·20	72·12
Potash and soda	21·41	16·31	20·04
Cobaltous oxide	6·49	6·75	1·95
Alumina . .	0 43	8·64	1·80
Ferrous oxide .	0·24	1·36	1·40
Arsenious acid .	trace	—	0·08
Water and carbonic acid .	0·57	0·92	0·46
	100·00	101·18	97·85

Smalt is a very permanent blue pigment, largely employed for the production of blue colours with vitreous substances and in painting, both for delicate and coarse work. It was formerly much used for colouring starch, paper, &c., but for this and many other purposes it is now almost superseded by the far less permanent artificial ultramarine.

Cobalt yellow consists of potassium cobalti-nitrite, prepared by the addition of potassium nitrite to a solution of a cobalt salt acidulated with acetic acid. Its composition varies with the proportions used and the strength of the solution. Erdmann and Sadtler state that when precipitated from a solution containing much acetic acid it consists of $K_3Co(NO_2)_6$ with a variable amount of water.

Cobalt yellow is a bright yellow crystalline powder, very free from impurities, unacted upon by cold water or cold acids, and but slowly blackened by sulphuretted hydrogen.

It forms a fine pigment for artistic purposes. When used for painting porcelain it produces the usual blue colour on baking, which, on account of the purity of the substance, is of great beauty.

Salts of cobalt. The soluble salts of cobalt are prepared by solution of the oxide, carbonate, or metal in the various acids. They are generally pink and deliquescent, forming pink solutions when dilute, but when dried, or in concentrated solution, they are blue. For this reason, solutions of nitrate and other salts of cobalt are used as sympathetic inks, such writing being almost invisible until brought near a fire, when the letters appear blue. They gradually reabsorb moisture and again become invisible. They are largely used for neutralising the yellow colour of porcelain, and giving a pure white body, the porous clay being for this purpose soaked in solution of cobalt salts.

When ammonia is added to a solution of a cobalt salt, oxygen is absorbed, giving rise under various conditions to many complex series of salts containing ammonia and different oxides of cobalt.

Cobaltous hydroxide is obtained by adding an alkali to a solution of a cobalt salt either as a blue or red precipitate depending upon the proportion of alkali. The red modification is more reactive than the blue compound : they are regarded by Hantzsch as ' chromo-isomeric ' modifications (Zeitsch. anorg. Chem. 1912, 73, 304).

Cobaltous chloride $CoCl_2$ is prepared by dissolving the oxide or carbonate in hydrochloric acid, and evaporating the solution. According to the temperature at which it crystallises, it may contain 6, 4, or 2 molecules of water of crystallisation, the latter at the higher temperatures.

Cobaltous chloride is soluble in water or alcohol. A strong solution, or a weaker solution containing strong hydrochloric acid, is of a blue colour.

Cobaltous sulphate $CoSO_4.7H_2O$ is prepared by solution of the oxide or carbonate in dilute sulphuric acid. It crystallises in red crystals, isomorphous with magnesium sulphate, soluble in 24 parts of cold water.

Cobaltous nitrate $Co(NO_3)_2.6H_2O$ is a red deliquescent crystalline salt prepared by dissolving the oxide in nitric acid. It is very soluble in water, the solution being used as a reagent in blowpipe analysis.

Combinations of cobalt, as resinate, oleate or linoleate, tungate, oleo-resinate and resino-tungate, are employed as driers. (*See* Krauss, 8th Int. Cong. Appl. Chem. 1912, 12, 127; Journ. Soc. Chem. Ind. 1912, 31, 938.)

Cobalt Carbonyls. Cobalt forms two carbonyls : , the *tetracarbonyl* $Co_2(CO)_8$, and the *tricarbonyl* $Co(CO)_3$.

Cobalt · tetracarbonyl. This compound is prepared as follows : cobalt oxalate is carefully heated until completely converted into the oxide. It is then washed free from traces of chlorides which hinder the formation of the carbonyl, and dried at 120°. The oxide is placed in the apparatus described under ' carbonyls,' and reduced to cobalt by means of hydrogen, at a temperature of 300° and a pressure of 5 atmospheres. After the reduction, the hydrogen is displaced by carbon monoxide, the pressure being increased and the temperature lowered For the production of the carbonyl, a minimum pressure of 40 atmospheres and a temperature of 150° is needed, and at pressures up to 250 atmospheres and temperatures between 150° and 250°, varying quantities of the carbonyl are collected in a tube attached to the outlet of the apparatus, and immersed in a freezing mixture.

The tetracarbonyl forms orange-coloured crystals of sp gr 1·73, which melt at 51°, and decompose above that temperature.

The molecular formula is $Co_2(CO)_8$. The compound is insoluble in water, but is soluble in most organic solvents, and in nickel tetracarbonyl. It is not attacked by aqueous acids but concentrated acids and the halogens decompose it, forming the corresponding salt, carbon monoxide, and hydrogen

$$Co(CO)_4 + H_2SO_4 = CoSO_4 + 4CO + H_2$$
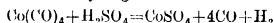
In contact with air a deep violet-coloured compound is formed, which is most probably a hydrated basic carbonate. The crystals are best preserved in a sealed tube in an atmosphere of hydrogen or carbon monoxide.

When the tetracarbonyl is heated at 60°, one quarter of the carbon monoxide is evolved at a regularly decreasing rate, leaving a compound having the formula $Co(CO)_3$ in the form of black cobalt and carbon monoxide, no intermediate product being formed.

When the tetracarbonyl is heated at 100°, one quarter of the carbon monoxide is evolved almost instantaneously, the rest coming off very irregularly and comparatively slowly (Mond, Hirtz, and Cowap, Chem. Soc. Trans. 1910, 97, 798).

COBALT BLOOM. *Erythrite*; *Hydrated cobalt arsenate* (*v.* COBALT).

COBALT BLUE or **THENARD'S BLUE** *v.* COBALT.

COBALT BRONZE *v.* COBALT.

COBALT GLANCE. *Sulpharsenide of cobalt* (*v.* COBALTINE).

COBALT GREEN or **RINMANN'S GREEN** *v.* COBALT.

COBALT PYRITES *v.* COBALT.

COBALT SPEISS *v.* COBALT.

COBALT ULTRAMARINE or **COBALT BLUE** *v.* COBALT.

COBALT YELLOW *v.* COBALT.

COBALTITE (or **Cobalt-glance**). Sulpharsenide of cobalt, CoAsS, containing Co 25–35 p.c. with Fe 2–5 p.c. It frequently occurs as well-developed crystals, fine specimens coming from Tunaberg and Håkansboda in Sweden and Skutterud in Norway ; these are cubic with parallel hemihedrism and with the same characteristic form as crystals of the isomorphous mineral iron-pyrites. Granular and compact masses also occur. The colour is tin-white with a reddish tinge and a brilliant metallic lustre ; the streak is greyish-black. Sp.gr. 6·2, hardness 5½ A bed of pure cobaltite averaging 0·2 metre in thickness occurs at Dashkessan, govt. Tiflis, Caucasus. In the Cobalt area of Ontario massive cobaltite and small crystals are present with the more abundant smaltite. Under the name *schta* the mineral, found at Kherti in Rajputana, is used by the Indian jewellers for producing a blue enamel on gold and silver.   L. J. S.

COCAINE AND THE COCA ALKALOIDS. The coca leaves of commerce are derived from *Erythroxylon coca* (Lam) (Bolivian or Huanuco), *E. coca* var. *novogranatense* (Morris) and *E. truxillense* (Rusby) (Peruvian or Truxillo coca).

Coca was introduced into Ceylon in 1870, and later into India, but whilst production in Ceylon attained considerable proportions, the Indian supply was never of commercial importance. Subsequently, cultivation was taken up in Java where, after considerable initial difficulties, production attained large proportions constituting about 45 p.c. of the world's supply, the remainder being produced in South America, Cultivation was stopped in Ceylon in 1915 by order of the Government.

Coca leaves contain alkaloids of four types :—
1. Cocaines ; alkyl acyl derivatives of ecgonine.
2. Acylecgonines ; acyl derivatives of ecgonine.
3 ψ-tropeines; acyl derivatives of ψ-tropine.
4. Hygrines.

The first and second types can be used as commercial sources of cocaine, since on hydrolysis they yield ecgonine which by benzoylation and methylation yields cocaine. The coca leaves derived from South America contain up to 1 p.c. of ether-soluble alkaloids (mostly cocaine), whilst Java leaves contain up to 1·5 p.c., or sometimes more ether-soluble alkaloid of which little or none is cocaine.

Estimation of total alkaloids in coca leaves.— The following process is given in the United States Pharmacopœia, 8th ed. : 10-grms. of coca leaves in No. 60 powder are mixed with 50 c.c. of a mixture of chloroform 1 vol., ether 4 vols., in a stoppered Erlenmeyer flask and set aside during 10 mins. Two c c. of ammonia solution, diluted with 3 c.c. of water, are then added, and the flask shaken at intervals during 1 hour. A small glass percolator with the lower end obstructed by a wad of cotton wool is then placed in the neck of a separating funnel containing 6 c.c. of N-sulphuric acid, diluted with 20 c.c. of water, and the contents of the flask poured into the percolator. When all the liquid has passed, the contents of the percolator are packed in firmly by means of a glass rod, and then the flask is rinsed out with 10 c.c. of the chloroform-ether mixture, followed by several successive washings with 5 c.c. quantities of the same mixture, the percolation being continued with

this liquid until 50 c.c. have been used in all. The separator is now shaken during one minute, the acid liquid drawn off, and the extraction repeated twice, using each time 10 c.c. of acid (6 c.c. N-acid with 20 c.c. of water); the combined acid liquors are made distinctly alkaline with ammonia solution and the alkaloids extracted with successive portions of ether (25, 20 and 15 c.c.). The ether is allowed to evaporate spontaneously, and the residue dissolved in 4 c.c. of N/10 sulphuric acid, and the excess of acid determined by N/50 potassium hydroxide using cochineal or iodeosin as indicator. This process gives the amount of ether-soluble alkaloids in the drug. No satisfactory process is yet available for the estimation of cocaine in the ' total alkaloids.'

Estimation of Ecgonine in total alkaloids -- The total alkaloids from 15-grm. of leaves are boiled for 1 hour with 30 times their weight of dilute hydrochloric acid; the mixture is cooled, extracted with ether, evaporated to dryness and the residual ecgonine hydrochloride weighed (Greshoff, Pharm. Weekb 1907, 44, 961)

Cocaine $C_{17}H_{21}O_4N$ occurs to a variable extent in the different varieties of coca leaves (*see* above).

Preparation —The coca leaves are exhausted by maceration and agitation with a mixture of aqueous sodium carbonate and petroleum, whereby the cocaine with *cinnamyl cocaine, &c*, passes into solution in the petroleum. The latter is shaken with dilute hydrochloric acid, when cocaine hydrochloride crystallises out and is collected, pressed and dried. This crude salt is purified by solution in water, liberation of the free base by ammonia, and solution of this in alcoholic hydrogen chloride, when the hydrochloride crystallises out. The mother-liquors contain the other coca alkaloids If Java coca leaves are used, the coca alkaloids other than cocaine alone are obtained, and these and the residual coca alkaloids referred to above are converted into cocaine by heating with boiling hydrochloric acid and pouring into water, when *truxillic and cinnamic acids* separate and may be filtered off. The filtrate is concentrated until ecgonine hydrochloride crystallises out. The ecgonine is recovered and then benzoylated and methylated in turn to produce cocaine.

The crude cocaine manufactured in Peru and imported to Europe for the preparation of cocaine salts is obtained by extracting the leaves with 0·5 p.c. sulphuric acid, making the filtrate alkaline with sodium carbonate and extracting with petroleum. The latter is again shaken out with dilute sulphuric acid and the crude alkaloid precipitated from this as a white, bulky powder by sodium carbonate. The powder is washed with water and dried by exposure to air for export.

Properties.—Monoclinic prisms, m.p. 98°; at higher temperatures it sublimes with decomposition. Laevorotatory [α]$_D$ − 15·8°; slightly soluble in cold water, more soluble in hot water, by which it is slowly hydrolysed. Soluble in alcohol, ether, benzene, light or heavy petroleum, or carbon disulphide. The aqueous solution is alkaline to litmus, has a bitter taste and produces a tingling and numbness of the tongue and lips, or, more generally, local anæsthesia of the surface to which it is applied.

On this account it is largely employed in minor surgical operations, although in recent years it has been replaced to some extent by synthetically prepared anæsthetics, such as benzamine (β-eucaine), stovaine, novocaine, &c. The alkaloid also causes dilatation of the pupil of the eye, but is not so powerfully mydriatic as some of the solanaceous alkaloids. When administered internally in small doses it acts as a stimulant, and diminishes the feeling of fatigue consequent on muscular exertion. Coca leaves have long been known to possess this property, and in places where the plant is abundant, a mixture of lime and coca leaves is chewed by the natives before engaging in severe exertion. Larger doses of the alkaloid are poisonous.

The ordinary salts of cocaine are crystalline. The *hydrochloride*, which is the salt used in medicine, forms white micaceous scales, possessing a characteristic lustre, or as white needles, readily soluble in water. The *chromate* $B·H_2CrO_4$, H_2O is thrown down, as a pale-yellow precipitate when potassium chromate is added to an acid solution of the hydrochloride. This salt is very slightly soluble in cold water, m p. 127°. The *aurichloride* $B·HAuCl_4$ is crystalline and sparingly soluble in water. When aqueous mercuric chloride is mixed with a solution of cocaine hydrochloride a bulky precipitate of the *mercurichloride* $B·HCl·HgCl_2.2H_2O$ is formed. This salt may be crystallised from alcohol. m.p. 124°.

d-Cocaine, m p. 46°, was obtained by Liebermann and Giesel (Ber. 1890, 23, 508, 926) from coca leaves, but was probably formed by the racemisation of *l*-cocaine by the action of alkalis; it has been synthesised from *d*-ecgonine. *dl*-Cocaine, m p. 80°, was prepared from *dl*-ecgonine by Willstatter and Bode (*ibid.* 1901, 34, 1457).

Detection.-- In isolating cocaine, the aqueous solution should not be heated for any length of time, and not at all in the presence of acids or alkalis. For the liberation of the alkaloid from its salts, ammonia, and not caustic alkalis, should be employed. Cocaine may be detected by its characteristic action on the tongue (see above). The following reactions are useful for the detection of the alkaloid : One c.c. of a 3 p.c. solution of potassium permanganate gives a violet precipitate with 0·01 grm. of the hydrochloride dissolved in two drops of water (Chem. Zeit. 1886, 10, 71 ; Amer. J. Pharm. 1911, 83, 195–201, 265–268). The hydrochloride heated with alcoholic potash gives off an odour of methyl benzoate. When moistened with nitric acid, the mixture evaporated to dryness and alcoholic potassium hydroxide added, a characteristic peppermint odour is produced.

The most important criteria of purity of cocaine hydrochloride are the m.p., the permanganate test, and the ammonia test.

The m.p. of cocaine hydrochloride varies with the rate of heating. When inserted into a bath previously heated to 195° and the temperature then slowly raised, it melts at 201°–202° ; when 3 drops of N/10 solution of potassium permanganate are added to 0·1 grm. of cocaine hydrochloride in 5 c.c. of water containing 3 drops of dilute sulphuric acid a purple colour is produced, which should show no diminution in shade in half an hour. If 0·1 grm. is dissolved

in 100 c.c. of water, 0·25 c.c. solution of ammonia added and the mixture set aside 15 minutes, the side of the beaker being occasionally gently rubbed with a glass rod, a crystalline deposit should be formed leaving the supernatant liquid clear (limit of amorphous alkaloids).

Reactions and Constitution.—Cocaine exhibits most of the general reactions of the vegetable alkaloids. When boiled with water it is gradually hydrolysed into methyl alcohol and l-benzoylecgonine (*see* below)
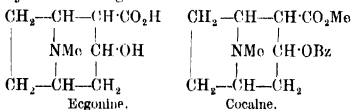
$$C_{17}H_{21}O_4N + H_2O = C_{16}H_{19}O_4N + CH_3OH$$

(Paul, Pharm. J. 1887–1888 [ii.] 18, 781; Einhorn, Ber. 1888, 21, 47), and the same change gradually occurs if the alkaloid remains in contact with an alkaline liquid. With alkalis or mineral acids methyl alcohol and benzoylecgonine are first formed, but the latter undergoes further hydrolysis into benzoic acid and l-ecgonine (see below).

$$C_{17}H_{21}O_4N + 2H_2O$$
$$= CH_3OH + C_7H_6O_2 + C_9H_{15}O_3N$$
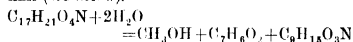
Natural cocaine is therefore methylbenzoyl-l-ecgonine

1-**Ecgonine** $C_9H_{15}O_3N$. This base does not occur as such in coca leaves, but is the ultimate basic product of hydrolysis of cocaine, cinnamyl-cocaine, the truxillines and benzoylecgonine. It crystallises from dry alcohol in monoclinic prisms with $1H_2O$, m p 140°, or 198°–199° (anhydrous); lævorotatory. It is readily esterified by alcohols yielding a series of alkyl esters, and by acid chlorides or anhydrides, giving the acylecgonines from which the corresponding ' cocaines ' are obtained by alkylation

Ecgonine is now known, principally as the result of the researches of Einhorn, Liebermann, Willstatter and their collaborators (*see* below), to be closely related to tropine, the ultimate basic hydrolytic product of atropine and hyoscyamine, and may be regarded as tropine-β-carboxylic acid Ecgonine and its most important derivative l-cocaine may be represented by the following formulæ :—

CH$_2$—CH—CH·CO$_2$H   CH$_2$—CH—CH·CO$_2$Me
│   │   │   │
  NMe CH·OH   NMe CH·OBz
│   │   │   │
CH$_2$—CH—CH$_2$ CH$_2$—CH—CH$_2$
     Ecgonine.   Cocaine.

Some of the chief papers bearing on the constitution of ecgonine are : Einhorn, Ber. 1889, 22, 399; 1890, 23, 1338; 1893, 26, 324; 1894, 27, 2823; Annalen, 1894, 280, 96; Liebermann, Ber. 1890, 23, 2518; 1891, 24, 606; Willstatter, *ibid.* 1897, 30, 702; 1898, 31, 1546, 2500, 2655; 1901, 34, 519; Annalen 1903, 326, 79.

1-**Benzoylecgonine** $C_{16}H_{19}O_4N$ is the first product of the hydrolysis of cocaine; it occurs in coca leaves from which it was isolated almost simultaneously' by Skraup (Monatsh. 1885, 6, 556), and by Merck (Ber. 1885. 18, 1594). The base crystallises from water in needles, m.p. 86° (anhydrous 195°), and is hydrolysed by hydrochloric acid to benzoic acid and ecgonine. On methylation it furnishes cocaine.

1-**Cinnamylcocaine** $C_{19}H_{23}O_4N$. This alkaloid is now known to occur in all varieties of coca leaves, but is found in largest proportion in the Java leaves, whence it was isolated by Giesel

(Pharm. Zeit. 1889, 34, 516). It forms needles, m.p. 121°, from benzene on addition of light petroleum. Lævorotatory. On hydrolysis it furnishes cinnamic acid, methyl alcohol, and l-ecgonine, and is therefore methylcinnamyl-l-ecgonine. The *d*-isomeride has been prepared (Einhorn and Deckers, Ber. 1891, 24, 7).

Truxillines $C_{34}H_{46}O_8N_2$. Two of these, α- and β-, occur in coca leaves ; the former is methyl-α-truxillyl-l-ecgonine, and the second the corresponding β-truxillyl compound (Hesse, Pharm. Zeit. 1887, 32, 407, 668 ; Liebermann, Ber. 1888. 21, 2342 ; 1889, 22, 130, 680). They are amorphous, and, according to von Liebreich, are heart poisons, and exert no local anæsthetic action.

Tropacocaine (Benzoyl ψ-Tropeine) $C_{15}H_{19}ON$ was isolated by Giesel (Ber 1891, 24, 2336) from Java coca leaves. It crystallises from ether, has m p 49°, is optically inactive, distils unchanged. The salts are crystalline, the *hydrochloride* melting at 283° and the *aurichloride* at 208°. On hydrolysis tropacocaine furnishes benzoic acid and ψ-tropine, and it may be prepared synthetically by the benzoylation of ψ-tropine (Liebermann, *ibid.* 1891, 24, 2336, 2587 ; 1892, 25, 927) ; the latter is a physical isomeride of tropine, and has been synthesised by Willstatter (Ber. 1896, 29, 936 ; 1901, 34, 129, 3163). who assigns to it the same structural formula as to tropine, and states that since tropine and pseudotropine are optically inactive the isomerism appears to be of the *cis-trans* type, a view subsequently confirmed by Barrowcliff and Tutin (Chem. Soc. Trans 1909, 95, 1970). Tropacocaine, like the pseudotropeines as a class, is almost devoid of mydriatic action, but like cocaine is a local anæsthetic, though the effect is more transitory.

Hygrines.—These secondary alkaloids were discovered by Lossen in Peruvian coca leaves (Annalen, 1862, 121, 374 ; 1865, 133, 352), and investigated by Liebermann and collaborators (Ber. 1889, 22, 675 ; 1891, 24, 407 ; 1893, 26, 851 ; 1895, 28, 578 ; 1896, 29, 2050 ; 1897, 30, 1113), who showed that Lossen's supposed homogeneous material contained two liquid alkaloids, one boiling at 193°–195° and having the formula $C_8H_{15}ON$, which makes it isomeric with tropine, and a second having the composition $C_{14}H_{24}ON_2$, b p. 215°, under 50 mm. pressure. The low boiling alkaloid is that now known as hygrine. Willstatter and Ettlinger's synthesis of hygrinic acid shows that hygrine probably has the following constitution (Annalen, 1903, 326, 91) :—

           ╱CH$_2$————CH$_2$
• Me·N
            ╲CH(CH$_2$·CO·Me)·CH$_2$
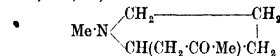
From ' cusco ' leaves Liebermann and Cybulski isolated a third substance of this type, viz. *cuscohygrine* $C_{13}H_{24}ON_2$, b.p. 185° under 32 mm. pressure, which forms a crystalline hydrate $B,3\frac{1}{2}H_2O$, m.p. 40°. It probably has the constitution (L. a. C., Ber. 1895, 28, 578)—

CH$_2$—CH$_2$ CH$_2$—CH$_2$
│   ╲CH·CH$_2$·CO·CH$_2$·CH╱   │
CH$_2$—NMe╱   ╲NMe—CH$_2$
                                S. S.
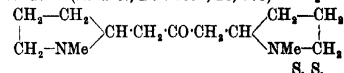
COCAETHYTIN. Trade name for the ethyl ester of benzoylecgonine.

COCATANNIC ACID v. TANNINS.

COCCINE v. AZO- COLOURING MATTERS.

α-COCCINIC ACID, COCCININ, v. COCHINEAL.

COCCULIN v. PICROTOXIN.

COCCULUS INDICUS or **INDIAN BERRY** is the fruit of the *Anamirta paniculata* (Colebar), [*A. Cocculus* (Wight and Arnott)] nat. ord. *Menispermaceæ*, a tree growing upon the coasts of Malabar, Ceylon, &c. The berry is about the size of a large pea and of a dark-grey colour It possesses strong poisonous and narcotic qualities from the fact of its containing about one-fiftieth part of its weight of picrotoxin, and has been employed to increase the bitterness as also the inebriating effect of beer It is, however, exceedingly deleterious to health, and the use of it for this purpose has been prohibited by the Legislature under heavy penalties.

Besides picrotoxin, Schmidt and Lowenhardt (Bull. Soc. chim. 14, 817) obtained from the seeds *cocculin* $C_{19}H_{26}O_{10}$, crystallising in white needles, sparingly soluble in hot water, insoluble in cold water, alcohol and ether. It is probably identical with Barth and Kretschy's *anamirtin* $C_{19}H_{21}O_{10}$ which they regarded as a constituent of picrotoxin.

Cocculus indicus berries contain *menispermine, paramenispermine,* and *picrotoxin* (v PICROTOXIN).

COCCUS CACTI, C. ILICIS, C. LACCAL. v. COCHINEAL.

COCHIN CHINA WAX v. WAXES.

COCHINEAL. This important natural dye-stuff, which, in its native country, Mexico, was used as a dye and cultivated by artificial means at a remote period of history, was for a long time considered to be of vegetable origin. Cochineal, however, consists of the dried body of an insect, the *Coccus cacti*, which lives upon a species of cactus (the *Nopalea coccinellifera* (S.-Dyck) or *Nopal*), a plant which is found in the wild condition, but which, for the sake of the insect, is cultivated in gardens which are termed *Nopaleries*. The collection of the insects takes place before the commencement of the rainy season, and they are then brushed either into straw baskets or into basins of tinned iron A number of insects are left upon each plant, and a new generation is produced, which is again gathered at a suitable period. The insects are killed by immersion in boiling water, or are enclosed in a linen bag and placed in an oven ; by the latter process the peculiar white down covering the insect is preserved, but in the former case is lost.

In Mexico and Central America two varieties of cochineal are known—the home-grown, or fine cochineal (*grana fina*), and the wild, or forest cochineal (*grana silvestra*). The former is more valuable than the latter, and is richer in colouring matter. Since 1830 the cultivation of cochineal was introduced into Spain and the Canary Islands, Algeria, and Java, but the most productive of these newer plantations were those of Java. Since the discovery of the coal-tar colours, the consumption of cochineal as a dye-stuff has gradually decreased, and at the present time it is only employed in a minor degree. According to Liebermann, cochineal contains about 10 per cent. of colouring matter (Ber. 18, 19).

Carminic acid, the colouring matter of cochineal, was first isolated by Pelletier and Caven-tou (Ann. Chim. Phys. (2), 8, 250), and was subsequently examined by Preisser (Annalen, 52, 375 ; J. Pharm. Chim. (3), 5, 191) and Arppe (Annalen, 55, 101); but Warren de la Rue (*ibid.* 64, 1) was the first to isolate this substance in a pure condition, and described it as a purple-brown mass, which, on grinding, yields a bright-red powder, easily soluble in water and alcohol, but not in ether. The mean of his analyses gave 54·13 p.c. of carbon, 4·62 p.c. of hydrogen, and 41·25 p.c. of oxygen (by difference), and from these figures he deduced the formula $C_{14}H_7O_8$ or $(C_{14}H_7O_8)_2$.

Schutzenberger (Ann. Chim. Phys. (3) 54, 52), on the other hand, was the first chemist who succeeded in obtaining carmine acid in a crystalline condition. He precipitated the colouring matter, from an aqueous cochineal extract, in the form of its lead compound, suspended this in water, and decomposed it with sulphuretted hydrogen. The carminic acid thus liberated dissolved in the water and was recovered from this solution by evaporation at a low temperature. The product, dissolved in alcohol, was treated with ether to precipitate certain impurities, and the liquid partially evaporated, when, on cooling, a crystalline mass was obtained, which Schutzenberger considered to consist of two substances, carminic acid, $C_9H_8O_5$, and oxycarminic acid, $C_9H_8O_6$, the latter being distinguished by its solubility in ether

Schaller (J. 1864, 410), who prepared carmine acid by the same method, assigned to it, however, the formula $C_9H_8O_6$.

The work of Hlasiwetz and Grabowski (Annalen, 141, 329) indicated that carminic acid was a glucoside which could be decomposed into a sugar and a new colouring matter, *carmine red*—

$$C_{17}H_{18}O_{10}+2H_2O=C_{11}H_{12}O_7+C_6H_{10}O_5$$
$$\text{Carminic acid} \quad \text{Carmine red.} \quad \text{Sugar.}$$
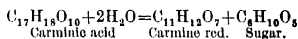
but according to Liebermann (Ber. 18, 1969 ; Will and Leymann, *ibid.* 18, 318 ; and Von Miller and Rohde, *ibid.* 26, 2647), this is incorrect.

Coccinin, according to Hlasiwetz and Grabowski, is produced when carminic acid is fused with caustic potash. It crystallises from alcohol in straw-yellow needles or leaflets, dissolves in alkalis with a yellow colour, which, by air oxidation, develops first a green, then violet, and, finally, a purple tint. The analyses of this substance were in agreement with the formula $C_{14}H_{12}O_5$.

Ruficoccin.—By heating carminic acid with sulphuric acid to 130°–140°C., Liebermann and van Dorp (Annalen, 163, 105) obtained a new colouring matter ruficoccin, $C_{16}H_{10}O_6$, and this consisted of a bright-red powder, sparingly soluble in hot water and ether, with a greenish-yellow fluorescence. On distillation with zinc-dust, it yielded a colourless crystalline hydro-carbon, $C_{16}H_{12}$, melting-point 183°–188°C., from which, by oxidation, a quinone melting at 250° C. could be produced.

Fürth, somewhat later (Ber. 16, 2169), prepared the same hydrocarbon by the distillation of both cochineal carmine and coccinin with zinc-dust.

Ruficarmine, $C_{16}H_{12}O_6$, can be obtained, according to Liebermann and van Dorp, by heating carminic acid with water in a sealed

tube at 200°C. It consists of a carmine-red powder, easily soluble in alcohol.

In view of the uncertainty existing as to the percentage composition of carminic acid, Schunck and Marschlewski (Ber. 27, 2980) submitted this substance to an elaborate process of purification, and, using in their operations as low a temperature as possible, obtained a product which crystallised from alcohol in red prismatic needles Their analyses agreed closely with that required by the formula $C_{11}H_{12}O_{6}$, and the percentage composition approximately with the figures given by Warren de la Rue, and also by Schutzenberger.

On the other hand, analyses by Miller and Rohde (Ber 30, 1762) pointed to the formula $C_{12}H_{11}O_{7}$ or $(C_{12}H_{11}O_{7})_{2}$, but according to the more recent work of Liebermann, Höring and Wiedermann (Ber 1900, 33, 149), it now appears that the correct formula for carminic acid is $C_{22}H_{22}O_{13}$.

The most simple method of purification of carminic acid is that devised by Miller and Rohde. A solution of the crude colouring matter in five times its weight of water is diluted with four times its volume of acetic acid. The filtered liquid, on standing over sulphuric acid, gradually deposits the carminic acid in a crystalline condition.

Carminic acid crystallises in red prisms, easily soluble in water and alcohol, with a purple-red colour. It possesses no melting-point. It darkens at 130°, and at 250° becomes quite black.

By the action of alcoholic potassium acetate, carminic acid (Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 139) yields two potassium salts, viz. :—

Monopotassium carminate $C_{22}H_{21}O_{13}K$, which is red coloured ; and

Dipotassium carminate $C_{22}H_{20}O_{13}K_{2}$, soluble in water with a violet-red colouration.

Hexabenzoylcarminic acid $C_{22}H_{16}O_{13}(C_{7}H_{5}O)_{6}$, obtained by digesting carminic acid with benzoyl chloride (Liebermann, Höring and Wiedermann), is an orange-coloured powder, easily soluble in benzene

Octacetylcarminic acid $C_{22}H_{14}O_{13}(C_{2}H_{3}O)_{8}$, crystallises in golden-yellow needles, melting-point 155°–165°, and is readily prepared by the action of acetic anhydride in presence of zinc chloride or sulphuric acid on carminic acid (Miller and Rohde).

Constitution of Carminic Acid.—Nitrococcussic acid was obtained by W. de la Rue from carminic acid by the prolonged action of boiling nitric acid. It was subsequently studied by v. Kostanecki and Niementowski (Ber. 18, 250), and was found to be identical with the *trinitrocresotinic acid*, of the following constitution :—
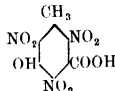

When carminic acid dissolved in 50 p.c. acetic acid is treated with an excess of bromine, and the solution digested at the boiling heat, two substances, known as α- and β-bromcarmines, are produced (Will and Leymann, Ber. 18, 3180).

α-*Bromcarmine* $C_{10}H_{4}Br_{4}O_{3}$, the more sparingly soluble substance, crystallises in colourless needles, and melts at 247°–248°, with decomposition. When oxidised with potassium permanganate in alkaline solution, it gives *dibrommethylhydroxyaldehydobenzoic acid*—
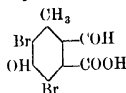

and *dibrommethylhydroxyphthalic anhydride*—
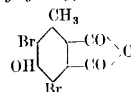
On treatment with hot caustic soda solution, α-bromcarmine yields, in addition to a purplered colouring matter, dibrommethylhydroxyphthalic acid, and *bromoform* (Miller and Rohde). As a result of this reaction, these authors assigned to α-bromcarmine the constitution of a *methylhydroxytetrabromdiketohydrindene*—
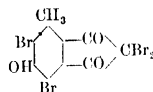

for Zincke (Ber 20, 3227 : 21, 2388) had previously shown that dibromdiketohydrindene itself—
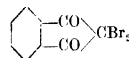
under similar treatment yields both phthalic acid and bromoform.

β-*Bromcarmine* $C_{11}H_{5}Br_{3}O_{4}$ is obtained as a yellow amorphous powder, easily soluble in alcohol (Will and Leymann), and is best purified by means of its potassium salt. Crystallised from acetone, it separates in orange needles, melting at 232° (Will and Leymann) or 288° (Miller and Rohde). By the action of bromine in the presence of 50 p.c. acetic acid solution, it is converted into α-bromcarmine. As a result of their investigation, Miller and Rohde ascribed to β-bromcarmine the constitution of a *methyldihydroxytribrom-α-naphthaquinone*, possessing one of the following formulæ :—

    or
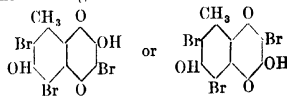
This suggestion was supported by the fact that bromoxynaphthaquinone (1), on treatment with bromine and caustic soda solution, is converted into dibromdiketohydrindene (2) (Zincke, *loc. cit*)—
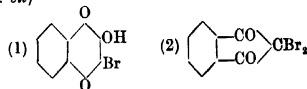

Additional support for this view was obtained by a study of the behaviour of β-bromcarmine

with zinc-dust in alcoholic solution. Thus the acetyl compound of the reduction product, melting-point 206°, gave, on analysis, numbers agreeing with those of the acetyl derivative of a *methyldibromdihydroxynaphthahydroquinone,* possessing the following formula :—
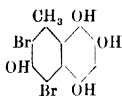
From a consideration of the points above enumerated, Miller and Rohde considered that the constitution of carminic acid could be represented by one or other of the following expressions :—
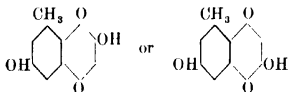

As, however, such formulæ require C=64·7 p.c., H=3·92 p.c., figures which are much higher than those given by the analysis of carminic acid itself, these authors suggested the addition of two molecules of water of hydration, as shown below—
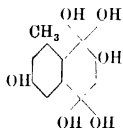
A substance of this constitution would require C=55 p.c., and H=5 p.c.

Somewhat later, Liebermann and Voswinkel (Ber. 30, 688) studied the oxidation of carminic acid with alkaline potassium permanganate at the ordinary temperature, and in this way succeeded in producing two important acids.

Cochenillic acid, $C_{10}H_8O_7$, crystallises in colourless needles, which melt at 224°–225° with evolution of CO_2. It is tribasic, and at 260° is converted into *hydroxymethylphthalic anhydride* (1). When heated with water in a sealed tube at 210° it yields symmetrical *cresotinic acid* (2)—
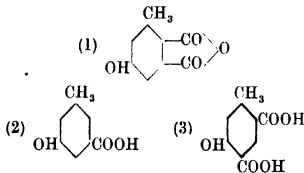

and in the same manner at a lower temperature, 170°, gives *a-coccinic acid* or *m-hydroxyuvitic acid* (3). The constitution of cochenillic acid is therefore as follows :—
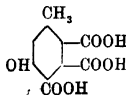
a-*Coccinic acid* $C_9H_8O_5$, the second product of the oxidation, which, as already indicated, can also be prepared from cochenillic acid, proved to be identical with the hydroxyuvitinic acid of Oppenheim and Pfaff (Ber. 7, 929). It consists of colourless needles, melting-point 239°.

Liebermann (*ibid.* 30, 1731), whilst agreeing with the diketohydrindene constitution which had been assigned to α-bromcarmine by Miller and Rohde, considered that β-bromcarmine was an indone rather than a naphthoquinone derivative, and could be better represented as follows :—
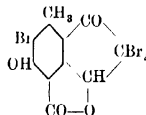

It was probable, indeed, that carminic acid itself was a hydrindene or bishydrindene derivative, and the following constitutions were at the time suggested for it—

or
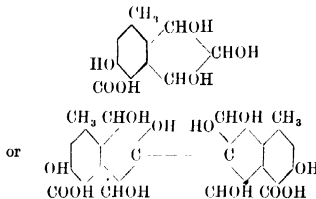
In a subsequent paper, however, Liebermann and Voswinkel (Ber. 37, 3344) consider that carminic acid is possibly a *tetrahydrate of a-dimethyldihydroxynaphthacenequinonedicarboxylic acid*—
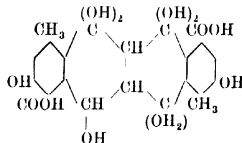

and it was observed that the dimethyltetrahydroxynaphthacenequinone—
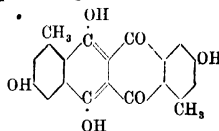
prepared by these authors not only possessed weak tinctorial property of a cochineal-like character, but in several respects closely resembled carminic acid itself.

Rohde and Dorfmüller (Ber. 1910, 33, 1363) further examined β-bromo-carmine, and obtained results which support the naphthoquinone constitution assigned to it by Miller and Rohde (*loc. cit.*), but disprove Liebermann's contention that it is a derivative of indone. By reduction with zinc-dust and acetic acid and subsequent

acetylation, β-bromo-carmine gives the compound $C_{17}H_{14}O_6Br_2$—
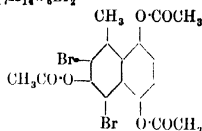
colourless needles, m.p. 208°C.

Simultaneous hydrolysis and oxidation converts this into the substance
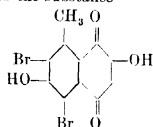
orange prisms, m.p. 258°C; and it thus appears that by the latter treatment an hydroxyl has entered the quinone nucleus. The diacetyl derivative melts at 233°C. When distilled with zinc-dust, this product, and also β-bromo-carmine itself, give naphthalene.

A valuable contribution to the subject was made by Dimroth (Ber. 1909, 42, 1611), who studied the oxidation of carminic acid with potassium permanganate at 0° in presence of sulphuric acid. The solution thus obtained gave nothing to ether, but on heating for three-quarters of an hour at 90°, it evolved carbon dioxide, and ether then extracted carminazarin.

Carminazarin crystallises from water in garnet-red needles, decomposing at 240°–250°. It possesses the constitution (1), and is very similar to *iso*naphthazarin (2)—
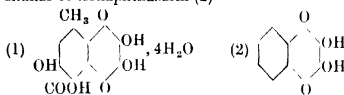
Its alkaline solution when treated with a stream of oxygen, is quickly decolourised with formation of 5 : 6-*dicarboxy-4-hydroxy-o-tolylglyoxylic acid*—
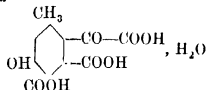

A further point of resemblance of carminazarine to *iso*naphthazarine is shown by its behaviour with nitric acid in glacial acetic acid, for whereas the latter gives tetraketotetrahydronaphthalene, the former yields the analogous *Carminazarinquinone* crystallising in colourless prisms—
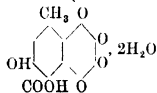

and which, when heated with water or acetic acid, passes back to carminazarin.

The intermediate product formed by the oxidation of carminic acid with permanganate at 0° insoluble in ether, and which, on heating, is transformed into carminazarin, is termed by

Dimroth *carminoquinone.* The constitutions assigned to this substance (1) and tentatively to carminic acid (2) are given below—
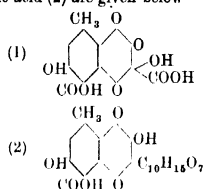

Carminic acid was, therefore, not a symmetrical compound, and the nature of the group $C_{10}H_{16}O_7$ was not then determined. At the time, Dimroth considered that the *coccinin* (see above) of Hlasiwetz and Grabowski, and which is prepared by fusing carminic acid with potassium hydrate, had probably the constitution of a *tetrahydroxymethylnaphthalene*—
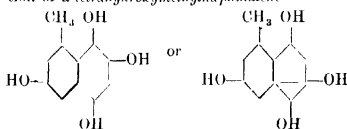

Later, Dimroth (Annalen, 1913, 399, 1) re-examined this product in detail, preparing it by fusing carminic acid with caustic potash at 170°–200°C. To it he gave the formula $C_{17}H_{14}O_6$, and described the pale yellow crystalline *tetra-acetyl derivative*, $C_{17}H_{10}O_6(CH_3CO)_4$, m.p. 242°–244°C.

When coccinin was oxidised by means of air, or oxygen, in alkaline solution (6 p.c. NaOH), the colour changes above described occurred, and when the pure violet colour had been obtained, acidification with hydrochloric acid yielded a substance *coccinone*, $C_{17}H_{12}O_7$, which forms dark brown glistening crystals and decomposes at 250°C; it yields a *tri-acetyl derivative*, $C_{17}H_9O_7(CH_3CO)_3$, orange-red crystals, m.p. 210°C., and also forms three different barium salts (one of which has a composition analogous to the sodium hydrogen salt of 2 : 6-dihydroxy-8-methyl-α-naphtho-quinone-3 : 5-dicarboxylic acid). Coccinone is reconverted into coccinin by reduction with zinc-dust and ammonia ; on the other hand, alkaline oxidation by means of hydrogen peroxide below 20°C. gives rise to two products, (i) cochenillic acid, and (ii) an unexamined acid.

Dimroth now formed the opinion that coccinin and coccinone are derivatives of anthranol and anthraquinone respectively, and the position of one of the hydroxy, methyl, and carboxyl groups in coccinone is made clear by the production from it of cochenillic acid. To coccinone Dimroth ascribes the structure—
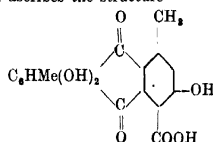
and to coccinin either the structure—

$C_6HMe(OH)_2$

OH   CH$_3$

—OH

H   COOH

OH   COOH

$C_6HMe(OH)_2$

—OH

H   CH$_3$
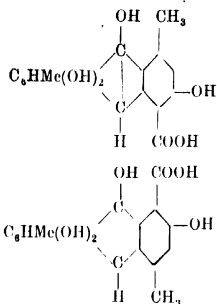
When heated with water at 200°— or dilute sulphuric acid at 170°C.— coccinone loses carbon dioxide, yielding *decarboxy-coccinone.* to which the structure—

O   CH$_3$

$C_6HMe(OH)_2$

—OH

O
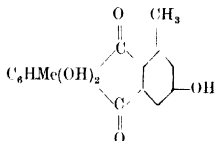
is given ; it forms red-brown crystals, and dissolves in alkalis to form purple red solutions and in concentrated sulphuric acid with a blue colour which becomes violet on addition of boric acid.

Not only coccinin, but carminic acid itself, has been further examined by Dimroth (*loc. cit.*), and as a result he considers that this substance is also a derivative of anthraquinone. He has oxidised carminic acid by means of hydrogen peroxide in aqueous caustic soda, using cobalt sulphate as catalyst, and in this way obtained in the first instance carminoquinone, but the reaction proceeded further with the formation, after acidification with 80 p.c. acetic acid, of a yellow crystalline compound, $C_{26}H_{13}O_{16}Na_3$, $5H_2O$, which, when triturated at 0°C. with dilute hydrochloric acid, yielded 2 : 6-*dihydroxy-8-methyl-α-naphthoquinone-3 : 5-dicarboxylic acid* : pale yellow, hygroscopic crystals—

CH$_3$ O

—OH

HO—   —COOH

HOOC   O
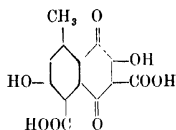
trisodium salt, $C_{13}H_6O_8Na_3,4H_2O$, orange needles.

The orientation of this acid has been established by Dimroth by comparison of its colour reactions with those of 2 : 6-*dihydroxy-α-naphthoquinone,* synthetically prepared by Dimroth and Kerkovius, as also by its conversion into carminazarin by treatment with acid permanganate. Moreover, the structure previously assigned by Dimroth to carminazarin, viz. 2 : 3 : 6-trihydroxy-8-methyl-α-naphthoquinone-

5-carboxylic acid, has been supported by conversion of carminazarin-quinone—the oxidation product of carminazarin—into a *diphenazin*, $C_{24}H_{14}O_3N_4$, by treatment with an alcoholic solution of o-phenylene-diamine. The product crystallises in yellow needles, and yields an *acetyl derivative,* $C_{26}H_{16}O_4N_4$.

When 2 : 6-dihydroxy-8-methyl-α-naphthoquinone-3 : 5-dicarboxylic acid—the oxidation product of carminic acid referred to above—is warmed with water, carbon-dioxide is eliminated with the production of 2 : 6-*dihydroxy-8-methyl-α-naphthoquinone-5-carboxylic acid* : brown-yellow needles—

CH$_3$ O

—OH

HO—

HOOC   O
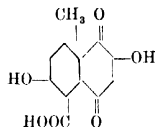
potassium salt, $C_{12}H_7O_6K$, lemon-yellow crystals ; *dipotassium derivative,* $C_{12}H_6O_6K_2$, orange-red crystals.

This compound when brominated in glacial acetic acid at 40° yields a *monobrom derivative,* yellow needles, m.p. 240°-244°.

CH$_3$ O

Br—   —OH

HO—

HOOC   O
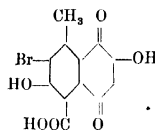
which on treatment with hydrobromic acid yields *α-bromo-carmin,* whilst with bromine in cold methyl alcohol, the product is *β-bromocarmin* (Will and Leymann), which proves that this body has the structure

CH$_3$ O

Br—   —OH

HO   —Br

Br   O
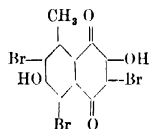
assigned to it by Miller and Rohde.

Beyond the above-mentioned decomposition products of carminic acid, Dimroth has obtained a 5 p.c. yield of hydrocarbons of the anthracene series by distillation with zinc-dust in an atmosphere of hydrogen. After oxidation of the mixture of hydrocarbons he isolated anthraquinone, and possibly α-methyl-anthraquinone.

By treatment of carminic acid with boiling dilute sulphuric acid, Dimroth has also obtained a 10 p.c. yield of trihydroxy-methylanthraquinone carboxylic acid ($C_{16}H_{10}O_7$), needles, melting-point above 300°, and this acid when heated with water at 230°-240°, passes into trihydroxy-methyl-anthraquinone by loss of carbon dioxide.

Dimroth considered the possibility that the anthraquinone nucleus is produced during the reactions described above, but concluded that this is not the case, and that it is present as such

both in carminic acid and coccinin. Dimroth formulates carminic acid thus—

$$C_{22}H_{22}O_{13} = \text{[structural formula]}$$
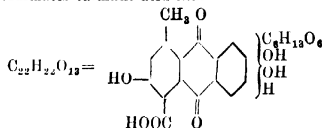
On the other hand, C. and H. Liebermann (Ber. 1914, 17, 1213) bring forward arguments, chiefly the smallness of the yield of anthraquinone or anthracene derivatives obtained by Dimroth, in favour of the view that the anthracene nucleus is formed during the degradation reactions.

These authors have also re-examined the 'ruficoccin' of Liebermann and van Dorp (see above), and conclude that it consists of a mixture of trihydroxy-methyl-anthraquinone carboxylic acid, and trihydroxy-methyl-anthraquinone, which is confirmation of the work of Dimroth Incidentally they described *carminic anhydride*, $C_{22}H_{20}O_{12}$, prepared by heating carminic acid with thionyl chloride—vivid red powder, resembling carminic acid, though less soluble. It is reconverted into the latter by the action of aqueous alkalis.

Technical Preparations of Cochineal.—Ammoniacal Cochineal—When a solution of carminic acid in ammonia is allowed to stand for some time, there is formed a new compound, which appears to consist of carminic acid in which one of the hydroxyls has been replaced by an amino group. The formula assigned to this substance by Schutzenberger was $C_9H_9NO_4$. This reaction, long known, has been utilised for the production of a new colouring matter termed *ammoniacal cochineal*, or *carminamide*, and thus comes into commerce either as cakes or in the form of a paste.

The first variety is usually prepared by allowing one part of cochineal to stand in a closed vessel for three months with three parts of ammonia. The clear liquid is decanted, treated with about half its weight of gelatinous alumina, evaporated, and when the mass has become thick, it is cut up into cakes and dried.

The paste is manufactured in a somewhat similar manner, the ammonia, however, being only allowed to react for eight days. The clear liquid is then evaporated to about one-third its bulk without addition of alumina (Crookes, Dyeing and Calico Printing).

Ammoniacal cochineal dyes much bluer shades than cochineal itself, and it is sometimes employed in conjunction with the latter. Its use is now very limited, but it finds some application in the blueing of bleached cotton.

Dyeing Properties of Cochineal.—Cochineal has been little employed in cotton dyeing, but was very largely used in silk and wool•dyeing. It has now been practically replaced by the azo-scarlets.

Two shades of red are obtained upon wool with cochineal, namely, *crimson*, which is produced by means of aluminium sulphate, and a very fiery *scarlet*, for which stannous and sometimes stannic chlorides are employed.

For crimson, wool is mordanted with aluminium sulphate and tartar, and is then dyed in a separate bath with cochineal. The employment of calcium salts in the dyeing operation is not beneficial. Fairly good shades of crimson can also be obtained by mordanting and dyeing in a single bath with aluminium sulphate, oxalic acid, and cochineal. For scarlet, wool can be mordanted with stannous chloride and tartar, and dyed in a separate bath with cochineal. A single-bath method, employing stannous chloride, oxalic acid, and cochineal, has, however, been very largely used for this purpose. On the other hand, preparations of stannic chloride, known as 'tin spirits,' 'scarlet spirits,' and 'nitrate of tin,' are and have been much employed by dyers of cochineal scarlet. Though, when used alone, stannic chloride does not give such brilliant shades as the stannous mordant, a mixture of both is considered to be beneficial. For very yellow shades of scarlet, yellow colouring matters can be added to the cochineal dye-bath, and of these 'flavine' has been employed to a considerable extent.

Cochineal red on wool possesses considerable fastness to light, but has the defect that weak alkalis and soap cause it to acquire a duller or more bluish shade.

Wool mordanted with potassium dichromate gives with cochineal a good purple colour, whereas with ferrous sulphate and tartar, purplish, slate, or lilac colours can be produced. These mordants, however, are not employed in practice A good crimson shade is produced by mordanting silk with alum, and dyeing with an extract of cochineal. In scarlet dyeing, silk is preferably first dyed yellow, then mordanted with 'nitromuriate of tin,' and finally dyed in a second bath with the assistance of cream of tartar. Silk can also be dyed in a single bath with cochineal, stannous chloride, and oxalic acid   A. G. P. & A. E. E.

COCHINEAL CARMINE *v.* LAKES.

COCHINEAL RED, SCARLET *v.* AZO-COLOURING MATTERS.

COCHINEAL WAX and **FAT.** The wax is obtained by extracting the cochineal with benzene, and consists almost entirely of a substance to which Liebermann gave the name *coccerin.* After the removal of the coccerin, the fat is extracted with ether ; it consists of myristin and an oil containing fatty acids. The following are the percentages of coccerin in various samples of cochineal (extracted whole with benzene) :

Silver cochineal	1·0	p.c
Mexican silver cochineal	1·7	,,
Teneriffe silver cochineal	2·0	,,
Zaccatille	0·5	,,
Teneriffe black cochineal	0·7–1·0	,,
Mexican black cochineal	1·5	,,
Granilla	4·2	,,

By powdering the cochineal before extraction, the percentage is increased by about one-half, except in the case of Granilla, where the granules are exceedingly small. The percentage of myristin is on the average about 1·5–2·0, and of fluid fat and fatty acids 4·0–6·0, so that the average total quantity of wax and fat contained in a silver cochineal is about 12 p.c. After recrystallising from benzene or acetic acid, coccerin forms thin glistening plates of melting-point 106°. It is sparingly soluble in all cold

solvents, and nearly insoluble in alcohol and ether. It has the constitution $C_{30}H_{60}(C_{61}H_{61}O_2)_2$. On saponification with alcoholic potash, it gives *cocceryl alcohol* $C_{30}H_{60}(OH)_2$ and *cocceric acid* $C_{31}H_{62}O_2$. The alcohol forms a white crystalline powder of m.p. 101°–104°. The acid melts at 93°, and is soluble in hot alcohol, benzene, &c. ; its ethyl ether melts at about 70°. The myristin $C_3H_5(OC_{14}H_{27}O)_3$ forms colourless crystals of m.p. 55°, easily soluble in warm alcohol, &c. ; on saponification it gives glycerol and myristic acid $C_{14}H_{28}O_2$ of m.p. 54°, and b.p. 248° at 100 mm (J. Soc Chem. Ind. 4, 585).

COCHINEALIC ACID *v.* COCHINEAL.

COCINIC ACID *v.* HENDECATOIC ACIDS.

COCOA. The cocoa tree is an evergreen shrub, indigenous to Mexico and the tropical regions of Central America, whence it was introduced into Europe by the Spaniards. It belongs to the natural order *Sterculaceæ*, and comprises several species, that most highly valued and cultivated being the *Theobroma cacao*, so called by Linnæus, from θεός (god) and βρῶμα (food), in allusion to the esteem and almost veneration in which the beverage prepared from its seeds was held by the natives of Central America, and ' cacao,' the name by which it was originally known. The seeds were used as a kind of money even down to the time of Humboldt's visit to Mexico.

The tree grows to a height of from 12 to 40 feet, the average being about 25 feet, but in plantations it rarely exceeds 18 feet It flourishes best in a moist and warm climate, in latitudes between 25° north or south of the equator, and at altitudes up to 1000 feet. It is now cultivated more or less extensively in Brazil, Caraccas, Central America, Ecuador, Essiquibo, Grenada, Guayaquil, Peru, Trinidad, Venezuela, and in the West Indies (particularly Jamaica, Dominica, and St. Lucia) ; also in Ceylon, the East Indies, the Philippines, Mauritius, Madagascar, San Thomé, Gold Coast, Cameroons, and to some extent in Australia.

The cocoa tree begins to bear fruit when 3 years old, and attains its full productiveness when 7 or 8 years old, but a healthy tree will bear for 40 or 50 years. Fruit is produced all the year round, but harvesting usually takes place only twice a year—from February to April, and again in October and November.

The fruit consists of an elongated pod, in shape between a melon and a cucumber, measuring from 5 to 12 inches in length, and from 2 to 4 inches in diameter, with a thick pericarp varying in colour from yellow or red to purple, according to the variety. There are from 20 to 40 or more seeds in a pod (though the number is smaller in the West Indian varieties) arranged in 5 longitudinal rows, and embedded in a rose-coloured mucilaginous pulp. When fresh they are usually white (some varieties purple), and have a bitter taste, but after drying and exposure to the air and light they acquire a yellow, red, or brown colour, and become hard, brittle, and less bitter. They are ovate, compressed, and about the size and shape of haricot beans or olives.

After removal from the pods, the seeds or beans are either freed at once from adhering pulp and dried in the sun (or occasionally by artificial means), to produce ' unfermented

cocoa,' or they are removed to the ' sweating ' or curing house to undergo a process of fermentation before drying. Unfermented cocoa is distinguished by its pale skin, which separates with difficulty from the kernel. Owing to its bitter taste, it is suitable only for use in cocoa mixtures containing starch and sugar. It is quite unfit for chocolate making, and commands a lower price than fermented cocoa.

To produce fermented cocoa, the beans were formerly buried in the ground, or in trenches covered with plantain leaves, but in order to avoid the consequent adherence of earthy matter, they are now generally buried in casks or boxes, or heated in piles in sheds, and turned over once or twice daily. The temperature rises considerably during fermentation, and the process requires great care and skill, as on it the commercial value of the finished beans chiefly depends.

In the fermentation—for which the optimum temperature is 35°–40°—alcoholic fermentation is succeeded on the second or third day by acetic fermentation ; during the subsequent drying, oxidation of the astringent constituents occurs. The market value of the seeds varies inversely as their tannin content. When the seeds contain over 20 p c of moisture butyric fermentation often occurs and causes mouldiness. Oxidation is most rapid at 50°–60°, but must not be allowed to proceed too far, or loss of aroma occurs. For observations on the fermentation of cocoa, *see* Brill, J. Soc. Chem. Ind. 1917, 36, 1245.

The objects arrived at in the ' sweating ' operations are the loosening of the adherent pulp, the removal or modification of the bitter principle, the development of an agreeable aromatic odour, and the colouration of the beans to a rich mahogany tint. The fermentation process generally lasts from 2 to 7 days. In some parts, as Trinidad and Jamaica, red earth is often employed to assist in the removal of the mucilage from the beans, which are afterwards rubbed clean and dried. Occasionally Venetian red is used to impart a uniform red tint to the finished beans.

As the fermentation process produces considerable change in the composition of the nibs it has recently been replaced by treatment with a 1 p c. solution of sodium carbonate for 10 minutes at 45°, whereby the beans are ' stabilised ' and sterilised. Cocoa prepared in this way is perfectly stable, and contains no pre-formed sugar. Theobromine is not present in the free state, but is formed together with sugar and tannin by hydrolysis (*v. infra*).

In the drying operation the beans are spread out in trays and systematically turned so as to expose every part of the bean to the light, and, when thoroughly air-dried, are in a suitable condition for shipment.

The preliminary processes of manufacture consist in (*a*) *sifting* out sand, dust, and small stones ; (*b*) *picking* out by hand the empty beans and foreign matter, as larger stones, grass, wood, &c. ; (*c*) *roasting* ; and (*d*) *cleaning*, by breaking up the beans and removal of the husks or shells. Berhardt (Chem. Zeit. 1889, 32) has found, from the results of actual factory work, that the losses in these operations amount to 2 or 3 p.c. in sifting ; nearly 1 p.c. in picking ; about

5 p.c. in roasting; and 12 or 13 p.c. in cleaning; making a total loss of over 20 p.c.

The roasting process, which requires great care, skill, and experience on the part of the operatives entrusted with it, is conducted in rotating cylinders heated by coke fires or by means of superheated steam in pipes lining the cylinders, to a temperature varying from 500° to 600°F. (160° to 315°C.). Uniformity of roasting is facilitated by grading the beans in the same operation to a uniform size The beans are then cooled, gently crushed in a 'kibbling mill,' to fracture the crisp husk and break down the kernel into its natural angular fragments or 'nibs,' after which the nibs, husks, and hard rod-shaped germs are separated by winnowing and sieving, and the nibs graded into different classes according to size.

The object of roasting is to develop to the fullest extent the characteristic aroma and flavour of the cocoa This is probably due to the development of a volatile principle in the nature of an essential oil, somewhat analogous to the caffeol of coffee (v. infra, Coca-red).

The roasted husks or shells constitute on an average about 12 or 13 p.c. of the weight of the whole bean, varying from 7 or 8 p c. in the thin-walled beans of Ceylon and Java to 18 p.c in those of Trinidad and the West Indies, which have a much thicker shell. The shells form a low-priced product extensively used, after grinding, in the cheaper grades of cocoa and chocolate, and occasionally, under the name of 'cocoa tea,' as a beverage which has the taste and flavour of weak cocoa Cocoa shells have proved to be a useful addition to feeding stuffs, especially for milch cows, and gave good results on the experimental farms of Canada when used as manure. (For analysis of cocoa shells, see table below.)

The nibs enter into commerce as such, but although in this form the consumer may be assured of the purity of the article, yet, owing to the large proportion of fat in them (about half their weight) and the difficulty of disintegrating them even by boiling water, they are hardly suitable for popular use as a beverage.

For the manufacture of the various forms of prepared cocoa, the nibs are ground by means of millstones or steel mills so constructed as gradually to reduce the cocoa to the finest and smoothest possible condition. If the cocoa is to go into consumption as ground nibs in powder, the stones or rollers are kept cool during the operation, but if, as is usual, the ground cocoa is afterwards to be made up into any of the numerous forms of prepared cocoa or chocolate, the stones or rollers are usually kept heated during the grinding. This causes the fat to melt, and the whole is reduced to a liquid mass, which is run into moulds and cooled so as to form blocks, which are sold as such or kept as stock for subsequent conversion into prepared cocoa or chocolate.

The leading types of manufactured cocoa are *flake cocoa*, *rock cocoa*, and cocoa powders sold under such names as 'soluble' cocoa, and 'extract' or 'essence' of cocoa. *Flake cocoa* is prepared simply by grinding the whole beans or the nibs only in steel mills somewhat resembling those used for grinding coffee. *Rock cocoa* is made in the form of a paste by grinding in a mill with heated stones or rollers, and with the addition of sugar and starch.

The admixture of starch or other gelatinising substance tends to mask the presence of the fat and to render the cocoa more readily miscible with boiling water. These mixtures, sold under such names as 'homœopathic,' 'Iceland moss,' &c., are frequently described as 'soluble cocoa,' but this is a misnomer, since the absence of a sediment in the cup is due, not to solution of the cocoa, but to the formation of an emulsion, which holds the cocoa in a finely divided state suspended in the liquid. In some of these, as 'granulated cocoa,' 'cocoatina,' &c, sugar is added as well as starch.

The large proportion of fat (about 50 p.c.), being found by many to be difficult of digestion, is reduced in preparations intended for use as a beverage, not only by the addition of sugar and starch (which incidentally reduces the proportion of cocoa present), but also by the actual abstraction of fat to form the so-called 'essence' or 'extract' of cocoa.

The partial extraction of the fat is accomplished by submitting the pure cocoa paste enclosed in strong canvas bags to a pressure of 1200–1400 lbs. per square inch in hydraulic presses heated to 70°–80°. The cocoa butter flows out through a special orifice, and is afterwards solidified into blocks or slabs ready for use in surgical and pharmaceutical preparations, for soap making, and in the manufacture of chocolate confectionery. The commercial value of cocoa butter just before the war was twice that of the raw bean, and this no doubt was an inducement to its removal, in addition to the alleged purpose of making the cocoa more digestible.

To prepare the so-called 'essence' or 'extract' of cocoa, the cakes of compressed cocoa, now containing only about 25 p.c. of fat, are turned out in a nearly dry condition, and ground to a fine powder. Some cocoa powders are said to be rendered more digestible by treatment with alkalis, which soften the cellulose tissue and act upon the fat so as to produce a more perfect emulsion than that obtained by other 'soluble' cocoas prepared with starch; also there is less tendency to separation of the melted fat in the cocoa beverage. Another method is to soften the tissue by heating in closed vessels with or without water to a temperature of 150°. In some preparations, as 'solidified cocoa,' the fat is not removed, whilst a preparation of cocoa practically free from fat is obtained by extracting the roasted and ground beans with ether or benzene. The ordinary flavouring materials are vanilla and cinnamon, but other spices and artificial vanilla are occasionally used.

The principal constituents of cocoa are fat ('cocoa butter'), alkaloids, albuminoids, starch, tannin, cocoa-red, and mineral matter.

The *fat*, *cocoa butter*, or *cacao butter*, *oleum theobromæ*, is the principal food constituent of cocoa, and forms from 45–55 p.c. of the husked bean. It has a pleasant taste and odour, suggestive of chocolate. At ordinary temperatures it is a yellowish-white, somewhat brittle solid, melting below the temperature of the body, viz. 28°–33°, and solidifying at 21°–23°;

sp.gr. from 0·95 to 0·97 at 15°, and 0·856 at 100°; iodine number from 33 to 38; saponification value, 193–195; refractometer reading (Zeiss) at 40° is 46–47·8; and index of refraction, between 1·4565 and 1·4578 at 40°. It is readily soluble in ether, chloroform, turpentine, and boiling alcohol, from which it crystallises out almost completely on cooling. Chemically, it is a mixture of the glycerides of stearic, palmitic, oleic, and arachidic acids (Benedikt, Analyse der Fette und Wachsarten). It is sometimes adulterated with such substances as coco-nut oil, cotton seed, and sesamé oils, stearin, tallow, and paraffin wax. Illipé oil is often used as a substitute for cocoa butter (which it closely resembles in certain respects) in the manufacture of chocolate.

ANALYSES OF RAW COCOA NIBS.

	Bell	Boussin-gault
Moisture . . .	5·23	7·6
Fat	50·44	49·9
Starch	4 20	2·4
Albuminous matter :		
Soluble . . .	6·30	} 10·9
Insoluble . .	6·96	
Astringent principle .	6·71	0·2
Gum	2 17	2 4
Celluloso . . .	6·40	10·6
Alkaloids . . .	0·84	3·3
Cocoa-red . . .	2 20	—
Indefinite organic matter		
(insoluble) . .	5·80	5·3
Ash. . . .	2·75	4·0
(Tartaric acid) . .	—	3·4
	100 00	100 0

Alkaloids.—Theobromine $C_5H_2(CH_3)_2N_4O_2$, or dimethylxanthine, is the principal alkaloid in cocoa, and is closely related to the alkaloid of tea and coffee, caffeine (trimethylxanthine), which is also present to a small extent in cocoa Theobromine crystallises in white microscopic needles, having a bitter taste, and is present in cocoa to the extent of about 1·5 p.c. The published analyses show variations from 0·4 to 3·3 p.c., due to the different methods of analysis employed. One of the best methods is that of Decker, as modified by Welmans and Fromme (Pharm. Zeit. 47, 789, and 858; and Apoth. Zeit. 18, 68). The caffein is usually included with the theobromine, from which, however, it can readily be separated by means of cold benzene, in which caffeine is soluble, but theobromine practically insoluble. The amount of caffeine varies from 0·1 to 0·3 p.c. (*see* art. THEOBROMINE).

According to Kreuz, the proportions of theobromine hitherto shown in published analyses represent only *free* theobromine. He maintains that part of the alkaloid is combined and is not extracted until the cocoa has been subjected to hydrolysis. By this method Kreuz found from 2·8 to 5·1 p.c. of theobromine in cocoa beans (Zeitsch. Nahr. Genussm. 1909, 17, 526–7).

Albuminoids.—These have been but little studied, but Stutzer (Zeitsch. angew. Chem.

1891, 368) has classified the nitrogenous constituents of cocoa as follows :—

(1) Non-proteids, substances soluble in neutral water solution in presence of copper hydroxide (theobromine, ammonia, and amino-compounds).

(2) Digestible albumen, insoluble in neutral water solution in presence of copper hydroxide, but soluble when treated successively with gastric juice and alkaline pancreas extract.

(3) Insoluble and indigestible nitrogenous substances.

According to Stutzer's analyses, the proportion of albuminoids in cocoa powder manufactured without chemicals is between 17 and 18 p.c., of which 10 p.c. is soluble or digestible albumen, the remainder (over 40 p.c. of the whole) consisting of insoluble and indigestible substances. Forster, however, maintains that the proportion of digestible albuminoids reaches as high as 80 p.c., his experiments being made on the human subject, whilst Stutzer's were conducted under laboratory conditions (Hyg. Rundschau, 1900, 314).

Starch, as in oleaginous seeds generally, is not very abundant. It has been variously estimated from 2 to 20 p.c. of the nib, but many of the results are too high, owing, no doubt, to the conversion of cellulose into sugar when the acid method for the starch conversion is employed. The diastase method is preferable in the presence of cellulose. The average amount of starch is from 4 to 5 p.c., or about 8 p.c. calculated on the fat-free bean. The starch grains are nearly spherical, with a very indistinct nucleus They have a tendency to unite in small groups of 3 or 4, and rapidly lose the colour imparted by iodine. The average size is about 0·005 mm.

Tannin.—An astringent principle resembling tannin exists in the raw bean, but, according to Mitscherlich and Bell, it is rapidly oxidised to 'cocoa-red,' to which the characteristic colour of cocoa is due. Bell (Foods, i. 79) states that this astringent principle is different from the tannin of tea and coffee, and that its rapid change to cocoa-red, even during the process of analysis, renders its quantitative estimation difficult. It is precipitated by basic acetate of lead, and can be obtained after removal of the lead by sulphuretted hydrogen. It gives a green precipitate with ferric chloride not unlike caffeic acid under similar treatment.

Cocoa-red is not present in the fresh seeds, which are nearly white, but arises from the oxidation of the natural tannin of the seed. It consequently appears in different quantities in different kinds of cocoa. On hydrolysis it decomposes into glucose, tannin, and a resinous substance. By many the peculiar taste and aroma of cocoa are associated with the formation of cocoa-red, which increases in amount during the process of fermentation, drying, and roasting, simultaneously with a corresponding increase in flavour, thought to be due to the development of a volatile principle or essential oil. Details of methods for its extraction and estimation are given in Zipperer (Die Schokoladen Fabrikationen) and Blyth (Foods).

Mineral matter.—The ash in cocoa nibs varies from 2·5 to 4·5 p.c., the average, according to Zipperer, being 3·6 p.c. in raw, and 3·9 p.c. in

the roasted kernels. The shells contain two or three times this amount. Approximately half the ash (which is rich in potash and phosphates) is soluble in water. The ash is naturally lower than the average when starch or sugar has been added, and higher when fat has been abstracted, or when the cocoa has been adulterated with husks or coloured with pigments. The shell is rich in alkaline carbonates and silica as compared with the nib. A high alkalinity in the ash of cocoa powders indicates treatment with alkalis as described in the preparation of the so-called 'soluble' cocoas. The composition of the ash of cocoa nibs and husks is shown in the table given below.

Whilst cocoa ranks higher than tea or coffee as a nutritious beverage, its value as a substitute for solid food has been greatly exaggerated. In its content of alkaloid and tannin substances, it stands midway between tea and coffee, and, like them, it should be considered a stimulating beverage rather than a true food.

The tables on p 313 will serve to show the composition of cocoa nibs, shells, the ash, and several kinds of commercial cocoas

Adulterants.—Besides sugar and starches (which have come to be considered as essential ingredients of certain proprietary cocoa preparations), the usual adulterants are foreign fats (particularly coco-nut oil) to replace the abstracted cocoa butter, farinaceous substances, ground cocoa shells, and pigments such as ferric oxide, ferruginous earth, &c. For the estimation of cacao shell, *see* Knapp & McLellan, Analyst, 1919, 2, which contains a bibliography on the subject.   J. C.

COCO-NUT OIL GROUP. Under this heading is grouped a number of vegetable fats which differ from all other vegetable fats by having high saponification values in conjunction with high Reichert-Meissl values. The considerable proportion of volatile fatty acids which the fats belonging to this group contain, brings them into relationship with the milk fats of mammals. They differ essentially from the latter, however, in that they do not contain any butyric acid. The high proportion of volatile fatty acids contained in the members of these groups differentiates them from other fats which are also characterised by high saponification values, but do not contain volatile acids.

The fats belonging to the coco-nut oil group are the following : (*a*) Muriti fat, from *Mauritia vinifera* (Mart.) ; *Acrocomia vinifera* (Oerst.) ; (*b*) mocaya oil, from *A. sclerocarpa* (Mart.) ; *Cocos sclerocarpa*, *C. aculeata* (Jacq.) ; *Bactris minor* (Gart.) ; (*c*) cohune oil, from *Attalea cohune* (Mart.) ; (*d*) maripa fat, from *Palma* (*Attalea*) *maripa* (Aubl.) ; (*e*) aouara-kernel oil, from *Astrocarpum vulgare* (Mart.) ; (*f*) palm-nut oil, from the kernels of *Elæis guineensis* (Linn. ; Jacq.) ; (*g*) coco-nut oil from *Cocos nucifera* (Linn.) and *Cocus butyracea* (Linn) ; (*h*) fat from *Cocos acrocomoides.*

It may be pointed out that aouara-kernel oil and palm-nut oil differ considerably from the corresponding fats contained in the fruit flesh surrounding the seeds (*see* PALM OIL).

All these fats are derived from trees belonging to the palm family. The two most important fats are coco-nut oil and palm-kernel oil. The latter will be described subsequently (*v.* PALM KERNEL OIL).

Coco-nut oil is the fat obtained from the kernels of the coco-nut, especially from those of the two species *Cocos nucifera* (Linn.), and *C. butyracea* (Linn.).

Cocos nucifera grows on all coasts and islands of the tropics ; in fact, it may be considered a cosmopolitan of the tropical coast-lines in both hemispheres. The coco-nut tree is indigenous to the islands of the Malayan Archipelago, whence the nuts were carried by sea currents towards the east to the Pacific Islands and the coasts of Central America, and towards the west to Ceylon and the east coast of Africa.

Being well protected by the ' coir ' (fibres), the seeds are able to germinate on all shores (islands and even coral reefs) where they may be deposited.

The coco-nut tree forms large forests, especially on the coast-line of Ceylon, Java, and the Philippines. On account of its manifold uses, the tree has been cultivated early in the history of mankind, and the fruits were, therefore, gathered, as it were, on a commercial scale, not only in the localities named, but also in the South Sea Islands, Madagascar, Mauritius, Ceylon, Zanzibar, the east and west coast of Africa, the Antilles, and the coast-lines of tropical South America.

Cocos butyracea is indigenous to Brazil, and yields, together with *Cocos nucifera* (as also with the other *cocos* species mentioned above), the chief quantities of coco-nut fats which are consumed locally. The coco-nut oil which is exported to Europe is mainly derived from *Cocos nucifera.*

The coco-nut tree flowers when about 6 or 7 years old, and begins to bear fruit from an age of 8 years up to an age of 60 years. The nuts contain a fleshy endosperm, built up from a milky juice, rich in oil At the period of maturity of the fruit the milky juice has disappeared almost completely, and the endosperm forms the well-known coco-nut kernel, inside which the remainder of the milky juice, coco-nut milk, is enclosed. The kernel contains from 30 to 40 p.c. of fat, and about 50 p.c. of moisture.

Since the earliest times in the history of mankind, the kernels have been used by the natives of the South Sea Islands, and especially of India, as one of their chief articles of food. The mode of preparing the oil, as practised centuries ago, was of the most primitive kind. The kernels were cut into small pieces and exposed in piles to the sun, when the oil would run off spontaneously. Improved methods consisted in converting the kernels into pulp, placing the latter in vessels perforated with holes, and exposing them to the sun, when the oil would run through the holes. The oil was then collected and carried in bamboo sticks to the market, a practice which up till a few years ago still obtained in the outlying parts of the Philippines. In order to render the process independent of the heat of the sun, as in the rainy season, the kernels were, at a later stage of evolution laid on hurdles, formed from bamboo staves and coco-nut leaves, and dried over a slow fire, the fuel for which was derived from the shell of the kernels. In India, where the nuts became at an early date an extensively

used food product, the nuts were split into halves by a blow with a sharp instrument, the coco-nut milk was poured off, and the halves exposed to the sun to dry, whereby the kernels became readily detachable from the shell. The dried kernels were then triturated and expressed, or the pounded kernels were thrown into boiling water, when the oil rose to the top, and was ready to be skimmed off. The residual mass was used as cattle food (' coco-nut poonac '). This

COMPOSITION OF COCOA SHELLS (WEIGMANN).

Commercial varieties	Moisture	Nitro-genous sub-stances	Theo-bromine	Fat	Nitrogen-free extract	Cellulose	Ash	Sand	Total nitro-gen
Caraccas . . .	12·49	13·18	0·58	2·38	40·30	16·33	9·06	6·26	2·11
Trinidad . . .	14·64	14·62	0·74	3·45	44·89	15·79	6·19	0·42	2·34
Surinam . . .	13·93	16·25	0·78	2·54	42·47	17·04	6·63	0·85	2·60
Puerto Cabello . .	14·89	16·18	0·75	2·01	43·32	15·25	8·08	0·27	2·59

ROASTED BEANS AFTER REMOVAL OF THE HUSK (HEISCH).

—	Husk	Fat	Nitro-gen	Albu-minoids	Ash	Ash soluble in water	Ash soluble in HCl	H_3PO_4 in ash	Moisture	Starch, gum cellulose, &c.
Caraccas .	13 8	48·4	1·76	11·14	3·95	2·15	1·80	1·54	4 32	32·19
Trinidad .	15·5	49·4	1·76	11·14	2·80	0·90	1·90	0 93	3 84	32·82
Surinam .	15 5	54·4	1·76	11·14	2·35	0·80	1·85	1·23	3·76	28·35
Guayaquil .	11·5	49·8	2·06	13·03	2·50	1·75	1·75	1·87	4·14	30·47
Grenada .	14·6	45·6	1·96	12·40	2·40	0·60	1·80	1·35	3·90	35·70
Bahia .	9 6	50·3	1·17	7·40	2 60	0·90	1·70	1·26	4·40	35·30
Cuba . .	12·0	45·3	1·37	8·67	2·90	0·95	1·95	1·13	3·72	39·41
Para . .	8·5	54·0	2·00	12·66	3·05	1·40	1·65	1·00	3·96	26·33

ANALYSES OF THE ASH OF COCOA NIBS AND HUSKS (BELL).

—	1 Guavaquil nibs	2 Surinam nibs	3 Grenada nibs	4 Finest Trinidad nibs	5 Finest Trinidad husks
Sand . . .	—	—	—	—	5·12
Silica	0·15	—	—	—	2·87
Sodium chloride . .	0·46	0·53	0·57	0·65	0·44
Soda (Na_2O) . .	0 46	0·63	0·57	0·83	0·94
Potash (K_2O) . . .	23·35	28·00	27·64	29·30	37·89
Magnesia . . .	19·18	20·66	19·81	18·23	13·04
Lime	3·24	4·38	4·53	6·51	7·30
Alumina	0·10	0 04	0·08	0·08	0·55
Iron oxide (FeO) . .	0·21	0 38	0·15	0·10	0·63
Carbonic anhydride (CO_2) . .	0·69	3·31	2·92	4·19	10·80
Sulphuric ,, (SO_3) . .	2·77	4·29	4·53	3·91	3·25
Phosphoric ,, (P_2O_5) .	49·39	37·78	39·20	36·20	17·17
	100·00	100 00	100·00	100·00	100·00

The following table shows the general composition of commercial cocoas : —

ANALYSIS OF COMMERCIAL COCOAS (BELL).

—	Prepared cocoa	Iceland moss cocoa	Rock cocoa	Flake cocoa	Cocoa-tina	Choco-latine	Finest Trinidad nibs	Chocolat de Santé	Cocoa extract
Moisture .	4·95	5·47	2·58	5·49	3·52	4·40	2·60	1·44	5·76
Fat .	24·94	16·86	22·76	28·24	23·98	29·60	51·77	22·08	29·50
Starch (added)	19·19	24·70	17·56	none	none	none	none	2·00	none
Sugar (cane) .	23·03	29·23	32·20	none	none	none	none	61·21	none
Non-fatty cocoa	27·89	23·74	24·90	66·27	72·50	66·00	45·63	13·27	64·74
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

process was carried out with special care at Cochin and the coast of Malabar. Hence the reputation of Cochin coco-nut oil for best quality has been maintained to this day.

As large proportions of moisture left in the kernel readily lead to putrefaction, a further step in the preservation of the fat was found in drying the kernels thoroughly, so as to remove the bulk of the water. The absence of moisture rendered the growth of fungi impossible, and thus prevented excessive hydrolysis and subsequent rancidity. The process of producing the dried kernel—*copra*—developed into a manufacturing process.

Coco-nut oil became first known in Europe in the 18th century, but was not imported in any notable quantities before the year 1820 At present three qualities of oil are distinguished in commerce: (1) *Cochin oil*; (2) *Ceylon oil*; (3) *Copra oil.*

(1), *Cochin oil* represents the finest and whitest quality, and, is obtained as stated above, by boiling the kernels with water and skimming off the oil.

(2) *Ceylon oil* is prepared in a similar manner in the plantations of Ceylon This oil is not of such high quality as Cochin oil, owing mainly to the want of care on the part of the natives, as compared with that exercised by the natives of the Malabar coast Hence Ceylon oil represents, as a rule, a second quality of coco-nut oil, and is characterised by a somewhat higher percentage of free fatty acids than is found in Cochin oil At present, however, in some plantations in Ceylon, managed by Europeans, the same care is exercised as in Cochin, and some brands of Ceylon oil are now imported which yield little in quality to Cochin oil

(3) *Copra oil* is the oil prepared in modern factories in Europe, United States, Australia, from copra (*i.e.* the dried kernels), which are imported in enormous quantities into these countries. The conversion of the kernel into copra must not only be looked upon as a convenient method for reducing the cost of freight, but, as pointed out above, is pre-eminently a cheap process for preserving the coco-nut oil as far as possible.

In the Manila market copra oil is sold as ‘Cebu sun-dried,’ ‘fair marketable Manila,’ and ‘Laguna,’ but the distinction between the different grades is not well marked.

At present great care is bestowed on the preparation of copra; it is used in growing proportions for the production of edible coco-nut oil (*see* EDIBLE OILS), and coco-nut stearin (*see* CHOCOLATE FATS). In commerce we differentiate ‘sun-dried copra’ and ‘kiln-dried copra’ The sun-dried copra was considered the better quality, as it gives a white coco-nut oil, with only a slight yellow tinge, and could be readily converted into an edible oil. Kiln-dried copra is obtained by a more rapid process, the kernels being dried over a bamboo grating heated by burning underneath it the shells. In these primitive kilns, the fumes obtain ready access to the copra itself, and not only burn it occasionally, but impart to the copra a peculiar empyreumatic smell and a dark colour. Hence copra thus dried yields a yellowish oil which proves refractory in the refining process. At present, however, notable improvements are being introduced in the kiln-drying process (rotary driers, vacuum driers), so that it may be expected that in the near future kiln-dried copra will take its place next to, or rank equally with, sun-dried copra. Sun-dried copra contains on an average 50 p.c. of fat; in kiln-dried copra the percentage rises to 63 and even 65 p.c. Copra dried by means of hot air contains even as much as 74 p.c.

Its acidity (as oleic acid) should be less than 1 p.c. By reducing the amount of moisture to about 6 p.c immediately after opening the nuts the action of moulds is checked and a better yield of oil of good quality is obtained.

The copra is treated in oil mills in a similar manner to that in which oleaginous seeds generally are worked up The meal is expressed twice at a temperature of 55°–60°. The practical yield varies from 63 to 66 p.c , according the content of oil in the copra The expressed oil contains a notable quantity of free fatty acid, the amount depending on the quality of the raw material.

Copra press-cake is used for fertilisers and feeding-stuffs for cattle, but by separating the oil by appropriate methods a press-cake suitable for human food may be obtained. A meal suitable as a substitute for wheat flour and lard in pastry had the following composition: water, 7·35; oil, 32·14; ash, 4·05; crude fibre, 37·12; and proteins 20·34 p c. (Parker and Brill. Philippine J. Sci , 1917, A, 12, 87).

In our climate coco-nut oil is, at the ordinary temperature, a solid white fat of bland taste, having the peculiar, though not unpleasant, odour of coco-nut. The odorous substances in coco-nut oil consist chiefly, according to Haller and Lassieur (Compt. rend. 1910, 151, 697), of methylheptylketone and methylnonylketone These two ketones, together with certain undefined volatile substances, are removed in the process of refining coco-nut oil for edible purposes. In order to obtain coco-nut stearin (chocolate fat), the liquid glycerides are removed by expression in hydraulic presses, when 50-80 p.c. of the liquid glycerides are expressed. Inferior copra oils also are frequently subjected to the same process, and thus a commercial coco-nut stearin is obtained, which, on account of impurities, can only be employed in the manufacture of composite candles and night-lights. The lower qualities of coco-nut oil are used in enormous quantities in the manufacture of soap, whilst the best grades are used for margarine.

Coco-nut oil contains large proportions of myristin and, especially, of laurin, small quantities of palmitin, stearin, and triolein, and of caprin, caprylin, and caproin.

Elsdon (Analyst, 1913, 38, 8), using the method of alcoholysis, found coco-nut oil to contain glycerides of the following fatty acids in approximately the proportions named: caproic, 2; caprylic, 9; capric, 10; lauric, 45; myristic, 20; palmitic, 7; stearic, 5; and oleic acid, 2 p.c. Methods for the detection of coco-nut oil in butter are based on the large proportion of lauric and myristic acids in the fat (Shrewsbury and Knapp, Analyst, 1910, 35, 385; 1912, 38, 3).

The saponification value of coco-nut oil lies between 246 and 260; the Reichert-Meissl value

ot the oil is 7-8 ; its iodine value about 8-10 ; and its Hehner value 88 to 90. Owing to its peculiar chemical composition, coco-nut oil is not readily saponified by weak caustic leys. It requires for saponification alkaline leys of high strength, which, however, so easily convert it into soap, that it is only necessary to stir the fat and caustic alkali together at 30°–35°. and allow the mixture to stand. After a short time saponification takes place, with liberation of heat. (Soapmaking by the 'cold process.') Soaps so formed are very hard, and combine with a large amount of water without becoming soft. The soaps are further distinguished by their remarkable property of requiring large quantities of salt to throw them out of their aqueous solution. Hence they are used as 'marine soaps.' J. L.

COCOSITOL v. INOSITOL.

CODAMINE v. OPIUM.

CODEÏNE v. OPIUM.

CODEONAL. Trade name for a mixture of 1 part of medinal and 2 parts of codeïne-veronal.

COD LIVER OIL is obtained from the liver of the cod, *Gadus morrhua* (and of the dorsch, the young of *G. morrhua*, formerly considered a separate species, *G. callarius*). The cod appears annually at certain times in enormous shoals on the coasts of the northern seas, chiefly on the coasts of Norway, Scotland, Newfoundland, the east of the United States and of Canada, the west coast of the United States and the coasts of Japan and Siberia. The best-known and oldest fishing-grounds are those of Norway, where the fish make their appearance at regular intervals of the year

In the early years of the manufacture of cod liver oil, the livers were heaped up in barrels and allowed to undergo a process of spontaneous putrefaction, whereby the liver cells burst and the oil exuded. The oil so obtained was contaminated with decomposition products of the liver, and possessed that rank odour and nauseous taste with which even nowadays popular prejudice associates medicinal cod liver oil. Of late years the manufacture of cod liver oil has been carried out in a scientific manner, and the best oil is at present obtained by steaming the livers in the freshest state obtainable. The livers are washed immediately they are taken out of the body of the fish, and are placed in jacketed vessels in which they are heated to a temperature of 70°–80°, when the cells burst and the oil flows off. This oil is known as 'raw medicinal oil,' and is consumed as 'congealing oil' in those countries where the Pharmacopœia permits congealing oils. The British Pharmacopœia prescribes, however, a non-congealing oil, which will not 'set ' at the freezing-point It is prepared by expressing the fresh liver at a temperature not exceeding 85°, cooling the crude medicinal oil below zero, and filtering it at a temperature of about −5°. The 'stearine ' is sold as fish stearin of best quality for soap-making purposes. All unsound livers, and those which have been exposed for some time to the atmosphere, are then worked up for 'brown oil.' This oil is, of course, a genuine cod liver oil, but is (or should be considered) unfit for consumption, and is mostly used up in leather industries, under the name 'brown cod oil ' or 'cod oil.'

The pure medicinal oil is pale yellow or light yellow, and the best qualities have a slight fishy odour only, and a by no means unpleasant taste. Such oil has a sp.gr. of about 0·922–0·93 at 15°, and a saponification value of 175–192, and an iodine value of 140–175. The best qualities have an iodine value of about 175, for the longer the livers have been exposed, the lower will be the iodine value, so that this value alone may indicate, preliminarily, a good medicinal oil. The chemical composition of the cod liver oil glycerides is not yet completely known. Small quantities of palmitin occur in the oil, and are the cause of the separation of 'stearine.' The older statement that small quantities of lower saturated fatty acids, such as those of acetic, butyric, valeric, and capric acids occur in cod liver oil must be rejected, these statements being due to the fact that the cod liver oil in which those volatile fatty acids were found had already undergone decomposition The greater number of the liquid fatty acids in cod liver oil have not been identified. Among the unsaturated fatty acids there occurs undoubtedly *therapic acid*; this can be identified and isolated by means of its octobromide, $C_{17}H_{26}O_2Br_8$, which does not melt at 200°, and decomposes, with blackening above that temperature.

Japanese cod liver oil has a similar composition to that of the European oil. Specimens examined by Tsujimoto (Chem Rev Fett Ind. 1913, 20, 70) had sp gr. 0 9263–0·9290 ; saponification value 183·8–188·1 ; and iodine value 159·1–160·8. The fatty acids yielded 34·4–36 17 p c of therapic octobromide.

The therapeutic value of cod liver oil which was attributed to the organic bases occurring in badly rendered cod liver oil must (in the author's opinion) be ascribed rather to the easy manner in which cod liver oil is digested than to any specific constituent, for the purest cod liver oil practically represents a mixture of pure glycerides with a small amount only of cholesterol and other unsaponifiable substances.

Like all liver oils, cod liver oil may be identified by the colour test which it gives with concentrated sulphuric acid in a solution of carbon tetrachloride or carbon disulphide. The better the quality of cod liver oil the fainter is the sulphuric acid colour test : thus points to the fact that the colour test is due to small quantities of foreign substances which are dissolved by the oil from the tissues of the liver. This is borne out by the fact that when completely hydrogenated, cod liver oil no longer gives any colour reaction with sulphuric acid. A specimen of such fully hydrogenated oil prepared by Mannich and Thiele (Ber. deut. Pharm. Ges. 1916, 26, 36) melted at 65°, and had iodine value 1·2, and saponification value 186·2. J. L.
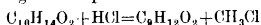
CŒLESTIN v. STRONTIUM.

CŒLINE, CŒRULEAN BLUE, CŒRULEUM v. COBALT ; also PIGMENTS.

CŒRULEÏN, *Anthracene green* (v. ALIZARIN AND ALLIED COLOURING MATTERS).

CŒRULIGNOL, $C_3H_7C_6H_3(OH)OCH_3$. A colourless oil of a burning aromatic taste, and a smell resembling creosote, obtained from beech pine and fir tars. Boils at 240°–241° ; sp.gr. 1·0564 at 15°. It is somewhat soluble in water, freely soluble in alcohol, ether, and acetic acid, It is coloured red by sulphuric acid, and

dark-brown by potassium hydroxide in contact with the air. In alcoholic solution it gives with barium hydroxide a characteristic deep-blue colouration. Ferric chloride in alcoholic solution gives a green, in aqueous solution a deep-red, colouration. Cœruhgnol is decomposed on treating with hydrochloric acid at 145°, according to the equation

$$C_{16}H_{14}O_2 + HCl = C_9H_{12}O_2 + CH_3Cl$$

CŒRULIGNONE (*Cedriret*).

$$(CH_3O)_2C_6H_2\cdot O\cdot O\cdot C_6H_2(CH_3O)_2$$
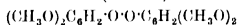
A steel-blue crystalline solid obtained by oxidising pyrogalloldimethylether in acetic acid solution with potassium dichromate (Hofmann, Ber. 11, 335) It combines with primary amines to give deep-blue dyestuffs (Liebermann and Flatau, *ibid.* 1897, 234 ; Moir, Chem Soc. Proc. 1906, 110 ; 1907, 307) (*v.* CEDRIRET).

COFFEE. The beverage known as 'coffee' is prepared from the seeds (dried, roasted, and ground) of *Caffea arabica* (Linn), an evergreen shrub, indigenous to North-East Africa, and Arabia. The use of coffee has been known from time immemorial in Abyssinia, whence it spread to the neighbouring Mahometan countries (where its use was at various times forbidden as being an 'intoxicating' beverage), and subsequently to all parts of the civilised world. It did not find its way into Europe, however, until the beginning of the 17th century It was introduced into England in 1652, and rapidly spread in popular favour in spite of heavy taxation and attempts to suppress the 'coffee houses,' for political reasons, until its importation reached a maximum of 37½ million lbs. in 1847. Since then the consumption has declined, due, no doubt, chiefly to the greatly extended use of tea, and partly to the introduction of coffee substitutes. At the present time the consumption of coffee in the United Kingdom is less than 30 million lbs , or less than ⅔ lb. per head. In the principal coffee-drinking countries of the world the consumption of coffee per head of the population is as follows : Holland, from 14 to 15 lbs ; United States of America, 12 lbs. ; Scandinavia, nearly 12 lbs. ; Germany, 7 lbs. ; and France, 4 lbs.

The coffee tree belongs to the natural order *Cinchonaceæ*, which embraces, according to Lindley and Paxton, two species, *C. arabica* and *C. paniculata* (Aubl.). Other botanists distinguish many other species, as *C. micrpcarpa*, *C. umbellata*, *C. acuminata*, *C. subsessilis*, *C. laurina*, *C. racemosa*, *C. bengalensis*, *C. indica*, &c. Some of these are probably only varieties. However this may be, four species distinct from each other are now grown : (1) Arabian or Mocha coffee, having short upright branches with a brittle leaf, and seeds usually single in the berries. (2) Jamaica coffee, bearing longer and more pliable branches, a tougher leaf, and seeds almost always double in the berries. (3) East India or Bengal coffee, of which the leaf is smaller than the Jamaica variety, and the berry very small. (4) Liberian coffee (*C. liberica*) is taller and has larger leaves and fruit than the preceding varieties, but owing to its coarse flavour, it was not until recently of much commercial use. It has, however, rapidly attained importance on account of its hardy habit and

power of resistance to disease, and is now largely cultivated by grafting on to its stem the more delicate and highly esteemed Arabian coffee. Trees growing wild in the Cingalese jungle attain a height of 14–18 feet ; but under cultivation and subjected to systematic pruning, the plant rarely exceeds 6–9 feet. Within the tropics the coffee tree succeeds best at 1200–3000 feet above the sea-level, but grows at a height of 6000 feet When the mean temperature is about 70°, it may be grown as far as lat. 36°. It is cultivated in the West Indies, Mexico, Central America, Brazil, and Cayenne ; in Western Africa, Egypt, Mozambique, and Natal ; in Arabia, India, Ceylon, Siam, Sumatra, Java, Celebes, and other parts of the Eastern Archipelago, Fiji, and the islands of the Pacific. At the present time more than three-quarters of the world's supply comes from Brazil.

The coffee consumed in the United Kingdom comes principally from Costa Rica and British India as regards the finer qualities, and the inferior grades from Brazil.

The manner of forming plantations varies somewhat in different countries. The surface soil should be good and the subsoil not too stiff. Perhaps the best soil is that known in Brazil as 'terra roxa,' a topsoil of red clay 3 or 4 feet thick, with a subsoil of gravel Virgin forest land is as a rule found very suitable Shelter from wind is most important, and a wet soil is fatal. Steep slopes are unsuitable owing to rain wash. The loss due to this cause should be repaired by good manure, well-rotted dung and ground bones being the best. The young plants may be reared in nurseries, whence they are transplanted to their permanent position, or they may be gathered out of the old plantations ; the age at which this is done varies, as in Brazil where the shrub is usually two years old on its removal, or as in the West Indies where it is planted out at 6 months Fruit is produced in the fourth year, and continues to be gathered for several years.

The tree blossoms and bears fruit practically all the year round, and the fruit takes about 4 months to ripen. There is thus in some places an almost perpetual crop, but, as a rule, there are two principal harvest seasons in the year.

The coffee fruit consists of a bilobed berry somewhat resembling a small elongated cherry (by which term it is described commercially). The fleshy pericarp changes colour, as the fruit ripens, from green through yellow and red to a deep crimson. When dried, it blackens and becomes hard and brittle, resembling a shell or husk. Beneath the skin of the pericarp is a saccharine and somewhat glutinous pulp containing the seeds, which are usually double, lying face to face, but sometimes occurring singly. Each seed or ' bean ' is enclosed in two membranous coverings—an outer, consisting of tough buff-coloured tissue, technically known as ' parchment,' which becomes loose and readily separates on drying ; and an inner film of thin white tissue, closely adherent to the bean, and known as the ' silver skin.'

The principal methods in vogue for gathering and preparing the coffee berries for commerce are as follows. In Arabia, Egypt, and the Antilles, the berry is left on the tree till completely dried,

when it is easily shaken down and the dry outer envelope and the parchment removed by pounding in a mortar, beating with a flail, or simply rubbing in the hands. In many other places the berries are gathered by hand as soon as ripe but not dry, and are spread out on the ground in layers from 4 to 6 inches deep. These are exposed to the sun's heat for 3 or 4 weeks, with frequent turning by means of spades, when the bean becomes easily removable from the fruit by gentle trituration. As this process of drying sometimes imparts to the coffee a disagreeable flavour owing to putrefactive changes in the pulp, recourse is frequently had to artificial heat. The most modern method is to 'pulp' the berries by crushing between rollers so as not to injure the beans, which are then subjected to a fermenting process in tanks, with or without the addition of water, after which they are separated from the pulp by 'washing,' and dried, either by the sun or by artificial means. Coffee beans in the form of 'cherry' rarely enter into commerce, but frequently retain the parchment and silver skin, which, however, before roasting, are removed by rollers and separated by winnowing. They are then graded into different sizes by special machinery, which also separates the round or 'pea-berries' from the ordinary flat-faced beans. The colour of coffee beans varies from a pale-yellow passing through various shades of green to a slatey grey. The following table will indicate the variations in size :—

	No. of seeds in a measure holding 50 grams of water.
Fine brown Java	187
Fine Mysore	198
Fine Neilgherry	203
Costa Rica	203
Good ordinary Guatemala	207
Good La Guayra	210
Good average Santos	213
Fine long-berry Mocha	217
Good ordinary Java	223
Fine Ceylon plantation	225
Good average Rio	236
Medium plantation (Ceylon)	238
Manilla	248
Ordinary Mocha	270
West African	313

Coffee undergoes important changes in the process of roasting, the object of which process is to develop its aroma and to destroy its toughness so that it may easily be reduced to powder. Great care is necessary to ensure an equable roasting of all the beans, and to attain the exact point at which torrefaction should cease. If, on the one hand, rawness is not removed, the flavour of the bean is not developed, and the coffee is hard to grind ; on the other hand, if too much heat is permitted, carbonisation takes place, and a strong empyreumatic flavour is produced, which renders the coffee infusion nauseous.

The roasting process is conducted in cylinders (preferably of strong wire gauze to permit of the escape of steam and other volatile products as fast as they are formed) heated by coke fires or gas. The loss in weight is from 15 to 18 p.c., of which about one-half is due to moisture, and the rest chiefly to volatile products derived from the fat, and from the sugar during the conversion of the latter into caramel. There is

also some loss of caffeine. At the same time, an empyreumatic oily substance is developed, known as *caffeol*, which, in spite of its small amount, imparts to roasted coffee much of its characteristic aroma. The most favourable temperature for developing the maximum aroma during roasting is a little above 200°. After roasting, it is most important that the beans should be rapidly cooled, and this is effected by spreading them on a large sieve through the meshes of which they cannot pass, but through which the air is forcibly drawn by means of a powerful exhaust connected with a closed chamber immediately below the sieve. Since the essential oil rapidly escapes after the bean is broken up, coffee should not be ground until required for infusion.

O. Bernheimer (Wien. Akad. 81, [2] 1032, 1042) found that during the roasting of coffee, water vapour is first given off, then suddenly an evolution of carbonic anhydride, and distillation of volatile substances commences. The distillate consists of an aqueous liquid and a solid part. The former contains caffeine, caffeol, acetic acid, quinol, methylamine, and acetone ; the latter consists of fatty acids, chiefly palmitic. Pyrrol escapes during roasting. Of fatty acids, 0·48 p.c. of the coffee employed was volatilised ; of caffeine, 0·18 p.c. ; and of caffeol, 0·05 p.c.

Erdmann (Ber. 1902, 35, 1846) attributed the aroma of roasted coffee to traces of acetic acid furfural, valeric acid, an unstable nitrogenous compound and a phenolic body resembling creosote. Various samples of roasted coffee yielded from 0·2 to 0·25 grm. of pyridine per kilo (Bertrand and Weisweiller, Compt. rend. 1913, 157, 212).

Bernheimer found that raw coffee beans (50 kg.) roasted in a revolving drum yielded a liquid distillate (5 litres) and a solid portion (680 grams) floating thereon. The uncondensable vapours contained carbonic anhydride, and, on passing them through dilute hydrochloric acid, a resinous body was deposited, having the appearance of pyrrol-red.

A. *Liquid distillate.*—The crude liquid distillate filtered from solid particles has a yellow colour and the fragrant odour of coffee. On agitating it with ether, and evaporating the ethereal extract over the water-bath, a dark heavy oil was obtained, smelling like coffee, and yielding, on redistillation, first a few drops of liquid having the odour of acetone, afterwards, for the most part, acetic acid and water. The thermometer then rose quickly to 200°, above which point there passed over an oil smelling like coffee, the temperature at the same time rising to 300°. Above this point there passed over a very small quantity of liquid, which immediately solidified to a mass having the buttery aspect and rancid odour of the higher fatty acids. This portion, and the liquid which passed over from 200° to 300°, were neutralised with sodium carbonate, whereupon a thick dark-coloured oil was thrown down, which was separated from the supernatant liquid by means of a tap-funnel, and washed with water rendered very slightly alkaline by potash.

The alkaline wash waters contained no fatty acids, but, when acidified with sulphuric acid and agitated with ether, they yielded a substance

which, after evaporation of the ether, filled the liquid with a pulp of crystals, and after precipitation crystallised in colourless needles, exhibiting the characters of *quinol* (m.p. 171°), converted into quinhydrone by the action of ferric chloride.

The oil above mentioned, designated by Bernheimer as *caffeol*, was dried over calcium chloride and fractionally distilled, the greater part passing over from 195° to 197°. The distillate smells very strongly of coffee, is apparently insoluble in cold water, but imparts to it the characteristic odour; slightly soluble in hot water, very slightly in aqueous potash, very easily in alcohol and ether, the alcoholic solution giving, with ferric chloride, a red colouration, which does not disappear on addition of sodium carbonate. Analysis led to the formula $C_8H_{10}O_2$. Caffeol is oxidised by chromic acid mixture, without formation of any definite products. By fusion with potash it yields salicylic acid. The portion of the crude liquid distillate not taken up by ether, when concentrated over the water-bath, yielded groups of needle-shaped crystals, exhibiting the composition and properties of *caffeine* $C_8H_{10}N_4O_2$ (0·28 p.c. of the coffee). The mother liquor was found to contain *methylamine* and *trimethylamine*.

B. *Solid distillate.*—The black mass floating on the crude liquid distillate was found, by a preliminary examination, to consist of a mixture of the higher fatty acids. By saponification, and treatment of the product by Heintz's method of separation, this mixture yielded, as chief constituent, *palmitic acid* melting at 60°, and a very small quantity of another acid having a melting-point a few degrees higher than that of lauric acid.

The chemical composition of coffee has been investigated by many chemists with various results. The following table gives analyses by O. Levesie (Arch. Pharm. [3] 8, 294) of some of the principal commercial varieties of coffee :—

	Gummy matter	Caffeine	Fat	Tannic and caffetannic acids	Cellulose	Ash	Potash	Phosphoric acid
Finest Jamaica plantation	25·3	1·43	14·76	22·7	33·8	3·8	1·87	0·33
Finest green Mocha	22 6	0·64	21 79	23 1	29·9	4·1	2·13	0·42
Ceylon plantation	23·8	1·53	14·87	20·9	36·0	4·0	—	0·27
Washed Rio	27·4	1·14	15·95	20·9	32 5	4·5	—	0·51
Costa Rica	20·6	1·18	21·12	21·1	33 0	4·9	—	0 46
Malabar	25 8	0·88	18·80	20·7	31·9	4·3		0·60
East Indian	24·4	1·01	17·00	19·5	36·4	—	—	-

Commaille (Mon. Sci. [3] 6, 779) found in undressed Mysore coffee :

Hygroscopic water (extremes
of 24 determinations) . . 6 3 to 15·7
Fatty matters . . . 12·68
Glucose 2 60
Dextrin . . . . —
Legumin-casein . . . 1·52
Albumen . . . 1·04
Total quantity of caffeine . 0 42 to 1·31
Ash . . . . . 3·882
Coffee extract with cold water 24·97
„ „ „ warm water 37·20
Coffee extract with alcohol of
60 p.c. . . . . 23·15

Dragendorff gives the following results of analyses of 25 different samples of coffee from Ceylon, Java, Malabar, Mocha, Mysore, and other places :—

	Maximum per cent.	Minimum per cent.	Mean per cent.
Caffeine	2·21	0·64	1·16
Ash	4 87	3·83	4·41
Phosphoric acid	0·72	0·28	0·42

The principal constituents of coffee are alkaloids (caffeine and caffearine), caffetannic acid, cellulose, fat, gum, protein, sugar, water, and mineral matter.

Caffeine $C_5H(CH_3)_3N_4O_2$, trimethylxanthine, is identical both chemically and physiologically with theine, the alkaloid of tea, and is closely related to theobromine (dimethylxanthine), the principal alkaloid of cocoa (*q.v.*). According to Payen (Ann. Chim. Phys [3] 16, 108), caffeine is present as a caffetannate, Gorter (Annalen, 1908, 358, 327) states that caffeine occurs in coffee combined with potassium as potassium caffeinechlorogenate $C_{42}H_{36}O_{12}K_2(C_8H_{10}N_4O_2)_2$, $2H_2O$. When pure it consists of white silky needles, slightly bitter and odourless, almost insoluble in ether, sparingly soluble in cold water and alcohol, but more soluble in hot water, and readily soluble in chloroform, by means of which it may be extracted from coffee. The crystals begin to sublime below the boiling-point of water.

Caffeine is found also in guarana leaves, kola-nut, maté or Paraguay tea and to a small extent in cocoa as well as in coffee and tea, and gives to these their exhilarating qualities. Taken in excess, caffeine is a poison. In coffee it is present to the extent of from 0·6 to 2·2 p.c., the average being 1·1 p c. Lendrich and Nottbohm (Zeitsch. Nahr Genussm. 1909, 18, 299) report nearly 3 p.c. of caffeine in certain African coffees, whilst in Madagascar and other islands off the east coast of Africa a variety of coffee has been found entirely devoid of caffeine. A coffee has recently been placed on the market after being deprived of practically the whole of its caffeine. *V* CAFFEINE.

Numerous methods have been proposed for the estimation of caffeine. That of Lendrich and Nottbohm is detailed in the Analyst, 1909, 214, and gives accurate results. A less tedious method, but sufficiently accurate for ordinary purposes, is that of Fendler and Stüber (Zeitsch. Untersuch. Nahr. Genuss. 1914, 28, 9–20) abstracted in the Analyst, 1914, 394.

Another alkaloid, *Caffearine*, having narcotic properties, is stated by Paladino (Gazz. chim. ital. xxv. 1895) to be present in coffee in very small quantity.

Caffetannic acid presents certain of the characteristics of tannin (which, however, is not found in roasted coffee) and to it the bitter taste of coffee is chiefly due. It is very susceptible to change, and its composition has been much disputed. According to Gorter (*vide supra*), it is a mixture of a new acid discovered by him and called *caffalic acid*, with chlorogenic acid. A method for its estimation in coffee has been devised by Krug (U.S.A. Dept. of Agric. Div. of Chem. Bull. 13, 908). According to Bell, caffetannic acid is present in coffee to the extent of from 3 to 5 p.c., and when distilled with manganese dioxide and sulphuric acid yields quinone.

Cellulose.—In coffee this is of a very hard and horny character, and difficult to define under the microscope, especially after roasting, although the chief characteristics of the cellular tissue are more or less retained. Coffee cellulose is dissolved by an ammoniacal solution of copper oxide, and gives a blue colour with sulphuric acid and iodine. Remnants of the 'silver skin' are always present even after roasting, and its structure, a thin membrane with adherent, thick-walled, spindle-shaped, and hollow cells, is quite peculiar to coffee.

Fat forms a considerable constituent of coffee, varying from 10 to over 20 p.c. A loss occurs in roasting, due to the separation of volatile fatty acids. When pure, coffee fat is white, inodorous, and of the consistency of butter, melting at $37 \cdot 5°$.

Protein, chiefly in the form of insoluble albuminoids, occurs in coffee to the extent of from 10 to 14 p.c., the soluble albuminoids constituting about 2 p.c. There is but little difference in this respect between raw and roasted coffee.

Sugar.—König and Bell found from 5 to 9 p.c. of sugar in raw coffee, but this practically disappears in roasting, being almost entirely converted into caramel. Herfeldt and Stutzer (Zeitsch. angew. Chem. 1895, 469) state that sugar is not present as such in the raw bean, but only in the form of a glucoside. Bell, however, found that when the saccharine extract of the beans is boiled with a little dilute sulphuric acid, a quantity of glucose is obtained nearly equivalent to the weight of dry extract operated upon, a result inconsistent with the existence of sugar as a glucoside. Bell considers that this sugar is not present as sucrose, since it is not inverted even after prolonged boiling with acetic acid. On the other hand, the chemists of the United States Department of Agriculture have isolated cane sugar in considerable amount as pure, well-defined crystals (*v.* Bulletin, 13). It is usually accompanied by some invert sugar probably formed during the process of extraction, and a small percentage of dextrin. Starch is rarely found in the coffee bean.

Water.—The moisture in raw coffee varies from 8 to 14 p.c., the average being about 11 p.c. After roasting, it rarely exceeds 3 p.c., and frequently falls as low as $0 \cdot 5$ p.c.

Mineral matter.—The total amount of ash varies from $3 \cdot 5$ to $4 \cdot 0$ p.c. in raw, and from $4 \cdot 0$ to $5 \cdot 0$ p.c. in roasted coffee. The composition of the ash is shown in the following table (U.S.A. Dept. of Agric. Div. of Chem. Bull. 13, 904):—

Constituents	Mocha	Maracaibo	Java	Rio
Sand	1·44	0·72	0·74	1·34
Silica (SiO_2)	0·88	0·88	0·91	0·69
Ferric oxide (Fe_2O_3) . . .	0·89	0·89	1·16	1·77
Lime (CaO)	7·18	5 06	4 84	4·94
Magnesia (MgO) . . .	10·68	11·30	11·35	10·60
Potash (K_2O) . . .	59·84	61·82	62·08	63·60
Soda (Na_2O). . . .	0·48	0·44	—	0·17
Phosphoric acid (P_2O_5) . .	12·93	13·20	14·09	11·53
Sulphuric acid (SO_3) . .	4·43	5·10	4·10	4·88
Chlorine (Cl) . . .	1·25	0·59	0·73	0·48
	100·00	100·00	100·00	100·00

The principal constituents are potash, magnesia, lime, and phosphoric acid. Ludwig, in his analyses of various parts of the Brazilian coffee tree, shows that the silica increases from the root upwards to the leaves and pericarp of the fruit, after which it declines in the parchment skin, and is nearly absent in the bean (Arch. Pharm. [3] 1, 482). Graham, Stenhouse, and Campbell inferred that sodium compounds are entirely absent in coffee (*vide* table in Bell's Food Adulteration, 46), but although this is not absolutely correct, the amount, as shown in the above table, is very minute.

Adulteration of coffee is very common, and the number and variety of the adulterants is almost unlimited.

Colouring is frequently employed in order to disguise damaged beans and give them the appearance of superior quality, a practice analogous to the 'facing' of tea. The substances most commonly employed are, for the raw beans, chrome yellow, yellow ochre, indigo, Prussian blue, azo- dyes, and soapstone for polishing; and for the roasted beans, burnt umber, oxide of iron, Venetian red, ferruginous earth and clay. The inorganic colouring matters are best sought for in the ash or in the sediment obtained by shaking the beans in cold water; indigo and

Prussian blue by their usual reactions ; and other organic colouring matters after extracting them with alcohol.

Glazing is a process resorted to for the alleged purpose of improving the keeping properties of the roasted beans, and the substances used, a mixture of egg albumen with glucose or gum, are said to have the effect of clarifying the infusion. The improved appearance of the beans and increased weight due to the retention of moisture, are probably also important considerations. The latter result is sometimes attained by the addition of sugar before roasting, or by actually steaming the beans and coating them with glycerine, palm oil, or vaseline, to prevent evaporation of moisture. Bertarelli (Zeitsch. Nahr. Genussm. 1900, iii. 681) describes the adulteration of roasted coffee beans with a solution of borax, which not only gives the beans a glossy appearance, but also adds as much as 12 p.c. to their weight.

Shellac is occasionally used for glazing, and Nottbohm and Koch draw attention to the fact that shellac is sometimes coloured by arsenic trisulphide. Coffee beans which had been glazed with arsenical shellac were found to be strongly contaminated with arsenic (Zeitsch Nahr. Genussm. 1911, 21, 288).

Coffee substitutes comprise a large number of vegetable substances, roasted and ground, and having for their object either the production of a stronger infusion than can be obtained from coffee alone, or the simulation of coffee in order to give weight by the use of thick-walled vegetable tissue of hard or leathery consistency. The former, of which chicory is the type, includes acorns, beet refuse, biscuits, bran, cereals (barley, buckwheat, maize, malt, oats, rye, and wheat) ; caramel (burnt sugar) ; carrots, dandelion root, figs, lupin seeds, mangolds, parsnips, peas, beans, and other leguminous seeds, turnip, &c. ; whilst the latter comprise such substances as coffee husks, cassia seeds, date stones, grape stones, locust or carob beans, sawdust, vegetable ivory dust, &c.

Imitation coffee.—Although adulteration is naturally more prevalent in ground coffee than in the beans, yet the latter have been prepared artificially and on a large scale from the above adulterants (generally without any admixture of coffee), held together by means of gum, molasses, or stiff clay, and skilfully moulded into the form of coffee beans.

The detection of the adulterants above referred to is best effected by means of the microscope. By simply digesting with water, a ready means is afforded of differentiating between the pale soft-walled tissues of cereals and roots and the dark-coloured and hard-walled tissue of coffee. The former may readily be detected and identified by the presence and characteristics of their starch, coffee (and chicory) being practically free from starch. The use of bleaching reagents is of great assistance in the microscopical examination, and reference might usefully be made to the drawings and photographs reproduced in the works of Bell, Leach, Villiers et Collin, and Wiley, and in the Coffee Report of Graham, Stenhouse, and Campbell, referrred to below.

The chemical differences between coffee and its adulterants are also strongly marked, as mixtures usually give high aqueous extract and sugar, and low fat and caffeine. The density is a useful factor in detecting the sophistication of coffee, and, in particular, the artificial moistening of the berries. In the Paris Municipal Laboratory, Regnault's volumenometer, as modified by Dupré, is used for this purpose. According to the French chemists, the density of raw coffee varies between 1·041 and 1·368, and that of roasted coffee between 0·500 and 0·635.

By far the most important adulterant of coffee is *chicory* (*q.v.*), but owing to the public preference for an admixture of chicory with coffee, it is now regarded in the light of an adjunct to rather than an adulterant of coffee, provided its presence in the mixture is disclosed. Chicory has little in common with coffee except a considerable proportion of sugar, which is converted into caramel in the roasting, and thus imparts to the infusion a bitter taste and aroma somewhat resembling that of coffee. This and the stronger infusion obtained as well as the comparative cheapness of chicory and similar substances, has, no doubt, led to the present extensive use of chicory and other coffee substitutes.

An elaborate research into the nature of coffee and chicory, with a view to the detection of adulteration, was made at the instance of the Commissioners of Inland Revenue in 1852 by some of the leading botanists and chemists of the day, viz. Lindley and Hooker, and Graham, Stenhouse, and Campbell, and the results, chemical and physical, as well as microscopical embodied in their reports are of great practical value even at the present time.

The following table by Graham, Stenhouse, and Campbell, shows the sp gr. at 60°F. of solutions made by treating one part of each of the substances named (roasted and finely ground) with 10 parts of water (by weight), raising the mixture to boiling-point, where it is maintained for half a minute, then filtering and cooling :—

SPECIFIC GRAVITIES OF SOLUTIONS AT 60°F.

One Part of Substance to 10 Parts of Water.

Spent tan	1002·1
Date stones	1002·9
Lupin seed	1005·7
Acorns	1007·3
Peas	1007·3
Mocha coffee	1008·0
Beans	1008·4
Neilgherry coffee	1008·4
Plantation Ceylon coffee	1008·7
Java coffee	1008·7
Jamaica coffee	1008·7
Native Ceylon coffee	1009·0
Costa Rica coffee	1009·5
Parsnips	1014·3
Carrots	1017·1
Black malt	1021·2
Turnips	1021·4
Rye malt	1021·6
English chicory	1021·7
Dandelion root	1021·9
Red beet	1022·1
Foreign chicory	1022·6
Guernsey chicory	1023·2
Mangold wurzel	1023·5
Roasted figs	1024·9
Maize	1025·3
Bread raspings	1026·3

It will be seen from the above table that the low sp.gr. of the coffee infusion distinguishes it from the roots and cereals, and when chicory is the only substance admixed with the coffee, its percentage may be calculated with approximate accuracy by a comparison of the density of the infusion of the mixture with the average densities of coffee and chicory given in the foregoing table.

The same observers lay stress on the relative colouring power of roasted coffee and chicory, the latter being four and a half times as great as the former. This property affords a simple device for detecting the presence of roasted chicory or other substances containing caramel when admixed with coffee. A few grains of the sample are placed on the surface of cold water in a glass, without stirring, when, if roasted chicory or similar substance be present, each particle omits a yellowish-brown coloured cloud, which is rapidly diffused in streaks through the water till the whole acquires a brownish colour, whilst pure coffee gives practically no colour to the water in similar circumstances. The chicory readily sinks, whilst nearly the whole of the coffee floats.

If examined under the microscope, the sediment of chicory which reaches the bottom of the vessel will be found to exhibit the characteristic loose, large cells, with dotted vessels and branching lactiferous ducts. Even to the touch the difference is evident, for, whilst chicory under these conditions will feel soft and smooth, the coffee grains remain hard and gritty.

A. Winter Blyth (Foods ; their Composition and Analysis, 359) gives the following summary of the influence of chicory on the coffee mixture :—

(1) It decreases the gum, the latter seldom rising in chicory to more than 15 p.c., whilst in coffee it has not been found less than from 21 to 28 p.c.

(2) It increases the sugar, roasted coffee having seldom so much as 2 p c. of sugar ; whilst chicory, when roasted, has at least 8 or 9 p.c.

(3) It decreases the fatty matter, the fat of chicory ranging from 1 to over 2 p.c., that of coffee being about 14 to over 20 p.c.

(4) It decreases the tannic and caffeotannic acids, chicory being destitute of tannin.

(5) It decreases the caffeine, chicory possessing no alkaloid.

(6) It profoundly modifies the constitution of the ash, especially by introducing silica, which is not found to any great extent in coffee ash.

Graham, Stenhouse, and Campbell laid stress upon the presence of silica as a means of detection of the admixture of chicory. Their analysis, showing the principal differences in the composition of the respective ashes, gives :

	In coffee ash	In chicory ash	
Silica and sand	—	10·69 to 35·85	
Carbonic acid	14·92	1·78 ,,	3·19
Ferric oxide	0·44 to 0·98	3·13 ,,	5·32
Chlorine	0·26 ,, 1·11	3·28 ,,	4·93

There is a marked difference in the proportion of ash soluble in water, that from coffee

amounting to from 75 to 85 p.c., and in chicory from 21 to 35 p.c.

Negro or *Mogdad coffee* consists of the seeds of *Cassia occidentalis*. It contains no caffeine nor starch, and its infusion more nearly approaches the character of genuine coffee than any other known coffee substitute.

Mussaendar coffee is derived from the seeds of *Gaertnera vaginata*. It contains no caffeine.

French coffee is a description commonly applied to a mixture of coffee with burnt sugar and a large proportion of chicory. As the latter ingredients readily absorb moisture on exposure to the air, such mixtures are usually preserved in tins.

Various fraudulent coffee substitutes have been imposed upon the public by specious advertising under fancy names, and as possessing certain desirable qualities not found in coffee. Such are *Kunst kaffee*, consisting of roasted roots or cereals, and often moulded into the form of coffee beans ; *Pelotas coffee* and *Coffee surrogate*, made from ground acorns ; *Date coffee* from date stones, or torrified dates mixed with a small proportion of coffee ; and many others.

The grosser forms of adulteration above referred to are much more prevalent in the coffee-drinking countries of the continent of Europe and in the United States of America than in the United Kingdom.   J. C.

COGNAC *v.* BRANDY.

COHUNE NUT FAT. The nuts of the Cohune Palm (*Attalea cohune*), indigenous to British Honduras, yield from 65 to 72 p.c. of a white solid fat resembling coco-nut oil. Sp.gr. at 100°/15·5° 0·868 to 0·871 ; acid value 1·2 to 20·4 ; saponification value 252·4–256·5 ; iodine value 11·0 to 13·7 ; Hehner value 87·7 ; Reichert-Meissl value 6·8 to 8·3 ; Polenske value 12·5 and 15·4. Solidifying point of fatty acids 19·7°–21·0° (Bull. Imp. Inst. 1913, 11, 226; 1914, 396).

COKE MANUFACTURE AND THE RECOVERY OF BY-PRODUCTS.

Introduction.—Previous to the early nineties, practically the whole of British metallurgical coke was made in the old beehive oven, which, as will be seen from what follows, is a semi-combustion process, involving the loss of the whole of the gas and by-products, together with a portion of the possible coke yield. With the gradual disappearance of the old prejudices against coke made in by-product ovens, the latter and much more economical process began to assert itself, and in 1898, 1·25 million tons of coal were being carbonised in by-product coke ovens ; in 1905 the quantity of coal so treated reached 3·31 millions ; and in 1916, about 14·60 millions. Meanwhile, the number of beehive ovens in operation had decreased from 16,037 in 1910, to 6892 in 1916. According to figures published by the Coal Conservation Committee at the end of 1917, some 8700 by-product ovens were in operation in Great Britain (of which 8000 were fitted with benzol recovery arrangements) with a total carbonising capacity of 17·5 million tons of coal per annum. In 1917, 166,354 tons of ammonium sulphate were produced in British coke-oven plants. The practice of by-product recovery had become universal in Germany years ago; whilst in the

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United States the by-product plants, either building or in operation at the end of 1917, were capable of producing 24 million tons of coke per annum. In view of this rapid adoption of the by-product coking process in all these countries, the following article will be confined to a description of modern coking methods viewed chiefly from a by-product standpoint, with only a passing reference to the wasteful beehive process.

History of the by-product coking process— The earliest reference which we can find of any observation being made on coal as a source of by-products is that contained in the memoirs of Johann Joachim Becher, dating about the end of the 17th century. Becher states that he has found means for treating coal 'so that it no longer smoakes nor stinks,' and in doing so made a tar equal to the Swedish.

The use of coke in iron smelting became general within 50 years of Becher's discovery, and a French metallurgist, De Gensanne, describes a process working at Sulzbach near Saarbrucken prior to 1768, where coal was coked for iron smelting, tar being recovered as a by-product; Stahl is said to have been the inventor of this process, and he produced therefrom an 'oil,' bitumen, sal-ammoniac, and lamp-black.

In 1781 Archibald, Earl of Dundonald, was granted a patent for 'allowing coals to burn or ignite without flaming, so by their own heat to throw off the tar or oils that they contain.' Dundonald stated that the only method whereby tars could be obtained prior to his discovery, was by a distillation in closed retorts, where the admission of external air was prevented, and where other coals were required for heating besides the coal contained in the closed vessel. It is interesting to note that Dundonald was perfectly aware of distillation in closed retorts, which is the basis of modern by-product coking methods, and it is also evident that his knowledge of closed retorts was 16 years previous to the introduction of coal gas for street and household illumination in 1797.

In 1838 Frederick Neville obtained protection for an invention which consisted in heating ordinary gas retorts by the waste heat from beehive coke ovens, the distilled gases from the retorts being passed though condensing and scrubbing appliances. William Newton, in 1852, introduced the use of an aspirator or pump for withdrawing the gases from coke ovens through condensers and rubbers. Newton likewise mentions the use of acids for removing the ammonia from the gases. In 1860 W. H. Kingston patented a coke oven provided with external furnace, from which the heat evolved by the combustion of an auxiliary supply of coal was conducted round the oven through a system of flues; the evolved gases were passed through a series of pipes and condensing vessels for the recovery of the by-products. Kingston's patent is especially noteworthy, since he recognises that the true method for the recovery of by-products from coal lies in heating the coal in closed chambers, and not in chambers to which air is admitted.

With regard to Continental practice, in 1850 M. M. Pauwels and Dubouchet, and in 1862, Pernelot, introduced systems of carbonising coking coals in long rectangular chambers, heated from below by the regulated combustion of part of the gas in flues specially constructed under the floor, for the purposes of manufacturing metallurgical coke and removing tars, oils, and ammonia. The Pernelot system was tried in the north of England in 1870, but the coke produced was too soft for metallurgical purposes.

In 1856 Knab erected a coal-distillation plant at Commentry, on the closed-retort system with bottom flues, but made no attempt to recover by-products. Later Knab was joined by Carvès, who (1866–1873) introduced improved methods of heating by side flues in addition to the bottom flues, thus obtaining a more even distribution of temperature and a quicker rate of carbonisation. Carvès likewise utilised the gases (from which the by-products had been extracted) in the side-wall flues, in addition to the auxiliary coal as employed by Knab. The Knab-Carvès ovens at Commentry gave the following results:—

Large coke	.	.	.	70 00
Breeze	.	.	.	1·50
Dust	.	.	.	2·50
Graphite	.		.	0·50
Tar	.		.	4·00
Ammoniacal liquor		.	.	9 00
Gas	.	.	.	10 58
Loss	.			1·92
				100·00

Further plants on the Carvès system were erected at Bessèges and Terre-Moire, near St. Etienne, between the years 1866 and 1873, and were still further improved; the Carvès ovens working at Bessèges in 1880 were built with carbonising chambers only 24 inches wide, to facilitate rapid heat penetration and quick carbonisation. In 1881 Mr. H. Simon of Manchester introduced a recuperator, whereby the air necessary for the combustion of the gas in the side-wall flues of the Carvès oven was preheated by the waste gases escaping from the flues, and thus the rate of carbonisation was still further increased; the combined work of the two investigators resulting in the well-known Simon-Carvès oven, which may be held to be the precursor of the modern by-product coking retort.

Following on the success of the Simon-Carvès process, other coke-oven patents were filed, viz. Semet-Solvay, 1880; Hussener, 1881; Lurmann, 1882; Otto and Brunck, 1883; but although development was rapid on the Continent, little was done in this country before the nineties, owing to the prejudice of iron smelters against by-product coke; that this prejudice has now disappeared will be seen from the rapid adoption of the process, indicated by the figures at the beginning of this article. The by-product coking plants which have generally found acceptance in this country are the Otto-Hilgenstock, Simon-Carvès, Koppers, Semet-Solvay, Simplex, Coppée, and Hüssener.

Non-by-product and by-product ovens compared.—Prior to the establishment of the by-product coking process, the type of oven universally employed was that known as the beehive.

This oven (Fig. 1) consists of a fireclay chamber, beehive shape in elevation and circular in plan, provided with a loose brick charging door at ground level, and with an exit flue in its crown for carrying the waste gases to the chimney. The coal is charged into the oven by spades, through the charging door, to a height of 2 feet 6 inches to 3 feet, is then ignited, and the charging door bricked up and plastered, a small hole 6 inches square being left for the admission of air. The upper layer of the coal burns and sets up distillation of the under layers, the evolved gases passing upwards and burning in the dome of the oven, with the air drawn in at the door. The dome is thus soon heated up to a high temperature, and by radiation powerfully assists in carbonising the charge of -coal below. This operation of distillation and immediate combustion proceeds until the whole of the volatile constituents of the coal have been evolved, which for a 10-ton charge occupies 70 hours. The coke is then quenched with water and withdrawn by rakes.

It will be seen that by this process, the whole of the volatile products, that is to say, benzols and ammonia together with the permanent gases, are burned immediately they are evolved within the coking chambers itself; further it is not possible to so regulate the combustion of these gases without burning a portion of the coke in addition; in actual practice, from 15 to 20 p.c. of the coke is burned to waste. For the reason, too, that the coke is quenched inside the oven, the temperature of the latter is lowered, so that before the next charge can be coked, considerable expenditure of heat is necessary to raise the oven to coking temperature. The removal of the coke by hand-rakes is also tedious and expensive.

With the object of overcoming the main drawbacks of the beehive oven, Coppée introduced a non-by-product retort of rectangular form, from which the coke could be discharged *en bloc* by a ramming machine and quenched outside the oven, thus expediting the operation and greatly increasing the yield. In Coppée's oven (Fig. 2) the gases evolved from the coal are drawn into flues in the side walls where they are burned, and in this way combustion within the coking chamber and loss of coke, as occurs in the beehive oven, is avoided.

The by-product retort (Fig. 3) is built on the same lines as the Coppée, that is to say, it is a rectangular chamber heated by flues in the side walls, and the coke is discharged by a ramming machine; the essential point of difference lies in the fact that in the Coppée the whole of the gases containing the by-products are drawn immediately they are evolved into the side-wall heating flues, where they are burned; in the by-product retort, the gases and products are drawn from the oven through cooling and washing plant for the recovery of the tars, ammonia, and benzol, and the permanent gas only is burned in the flues after the said products have been extracted. In the Coppée, the whole of the permanent gas is burned in the heating flues; in the by-product oven, only one-half to two-thirds of the gas is utilised in the flues, the remainder being available for heating or power purposes.

The following diagrams illustrate the essential differences in the three types of oven.
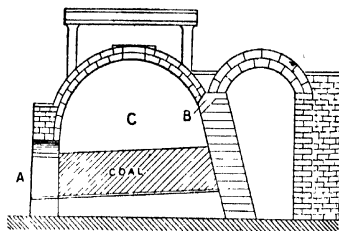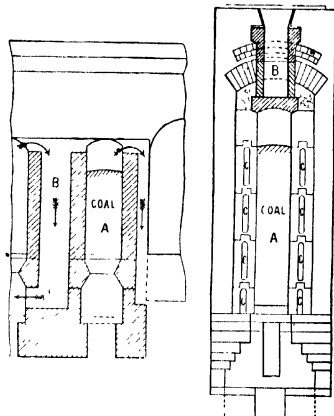

FIG. 1.—BEEHIVE.

FIG. 2.—COPPÉE.　　FIG. 3.—BY-PRODUCT RETORT.

It will be seen, therefore, that in addition to effecting the theoretical coke yield, and a large output, the by-product retort yields valuable by-products and a considerable yield of power or heating gas. The average yields (calculated upon 100 parts of *dry* coal) of coke and by-products obtainable from British coking coals of different origin by the most up-to-date methods, are approximately as follows :—

Origin	Coke	Anhyd tar	Crude benzol	Ammonium sulphate
Durham . .	75·0	3·85	0·93	1·16
South Yorkshire	70·0	3·62	1·37	1·35
Lancashire .	70·0	3·50	1·20	1·25
South Wales .	80·0	2·62	0·60	0·95
Scotland . .	68·0	3·25	0·70	1·00

The by-product process described in detail.— The by-product retort usually measures from 30 to 53 feet in length, from 5 feet 9 inches to 7 feet 6 inches in height, from 17 to 22 inches in width, and is built in batteries of from 25 to 60 ovens, capable of carbonising from 100 to 350

TABLE SHOWING THE RETURN FROM CARBONISING A LANCASHIRE COAL CONTAINING 30 P.C.
VOLATILE MATTER, *i.e.* A THEORETICAL COKE YIELD OF 70 P.C. IN THE THREE TYPES OF OVEN.

Beehive	Coppée	By-product retort
Combustion within coking chamber, quenching inside oven	Coking chamber heated externally by gas from which by-products not extracted : quenching outside oven	Coking chamber heated externally by gas from which by-products have been extracted : quenching outside oven
Yield of dry coke = 56 p.c. „ tar — „ sulphate of ammonia — „ benzol —	70 p.c. — — —	70 p c. 4 0 to 4·5 p.c. 1·0 to 1·2 p c. 2·5 to 3·0 gallons of crude benzol testing 62 p.c. at 120° per ton of coal
Waste heat— In most cases not utilised but approximately equal to 0·75 ton of water evaporated per ton of coal carbonised	Always utilised . equal to 1 ton of water per ton of coal carbonised	Always utilised · equal to 1 ton of water per ton of coal carbonised Surplus gas if required for other purposes than steam raising, *e.g* gas engines or furnaces, 3000 to 5000 cubic feet per ton of coal
Amount of coke produced per oven per week = 7 to 10 tons	24 to 26 tons	24 to 26 tons

tons of coal per day. Each oven is provided with cast-iron or rolled-steel doors at each end, lifted by a small crane whenever an oven is discharged, and with three holes in the roof through which the coal is charged into the oven from the charging hoppers ; a fourth hole is provided, through which the gases are led to an ascension pipe from which they pass to the by-product plant. The oven linings and combustion flues are constructed of silicious firebricks containing from 80 to 84 p.c. of silica, from 13 to 18 p.c. of alumina, and 2 p c. of other constituents (iron oxide, lime, magnesia, and the alkalis). In the United States, however, silica bricks (SiO$_2$=94 p.c.) are extensively employed. They are superior in heat conductivity to a more aluminous brick, but are less satisfactory when 'washed ' coals (containing say 10 to 15 p.c. water) are being coked The design of the heating flues constitutes the main difference between the various types of oven ; the Simon-Carvès, Semet-Solvay, Hussener, and Simplex containing horizontal flues ; the Otto-Hilgenstock, Otto-Hoffmann and Koppers prefer vertical flues (Figs. 4 and 5). In all cases the air required for the combustion of the gas in the heating flues is preheated either by passing it through recuperators in which it travels through a system of flues situated alongside the waste gas flues of the oven, or through regenerators similar to those employed in open-hearth steel furnaces, where the hot waste gases and air are alternately taken over the same surface (Fig. 6). Where a large supply of surplus gas is desired from a coking plant, the regenerative method of preheating the air is to be preferred, since it is more effective and less gas is required for heating the flues ; the amount of surplus gas available from a Lancashire coal containing 30 p.c. of volatile matter, may be taken at 2000 cubic feet per ton, where recuperative heating is employed,

and 5000 cubic feet per ton where regeneratives are used

The coal is generally charged into the oven through the crown from small hoppers, carrying the coal on rails from the storage bunker, the coal flowing into the oven being levelled by hand-rake or levelling machine. In cases where the coal employed is not of a strong coking character, the fuel is stamped into a solid cartridge in a compressing machine and charged into the oven *en bloc* through the end doorway, The coke is discharged from the oven by a ram, generally electrically driven, often the levelling machine or compressor is built on the same carriage as the ram, and driven by the same motor. The coke is received from the ovens on a sloping bench, where it is quenched with water, and from which it slides into railway trucks, furnace barrows, or a conveyor. The heating flues of each oven discharge into a common flue, which leads the waste gases in the case of recuperator types to steam boilers ; with regenerator-ovens, the gases are led direct to the chimney stack. The gases distilled from the coal collect above the level of the fuel and pass forward to the ascension pipe or stand pipe, which delivers the gas into the tar or hydraulic main, which receives the gases from the entire battery. A valve or damper is provided on each ascension pipe for shutting off each oven whilst the latter is being discharged and recharged. In the tar or hydraulic main the heavier tars or pitches are deposited, and in the ' dry ' types of main, it is necessary to pump the thinner tars made at a later stage of the cooling, through the main to clear the pitch and prevent stoppages.

In the older systems of by-product recovery, which are now being rapidly superseded by more ' direct ' methods (*q.v.*), the gases are drawn from the main by an exhauster (either
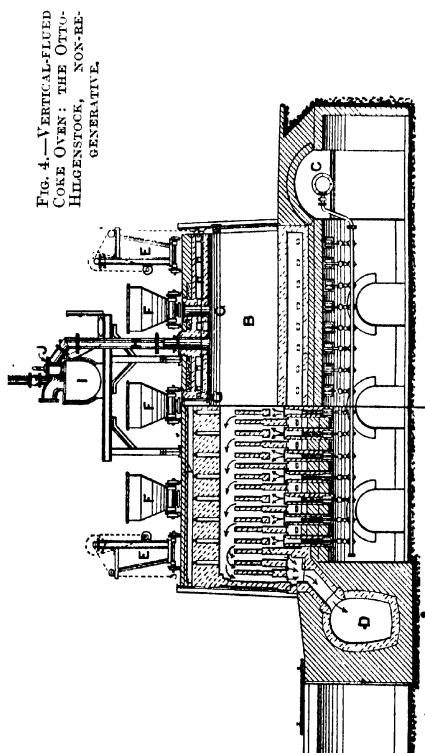
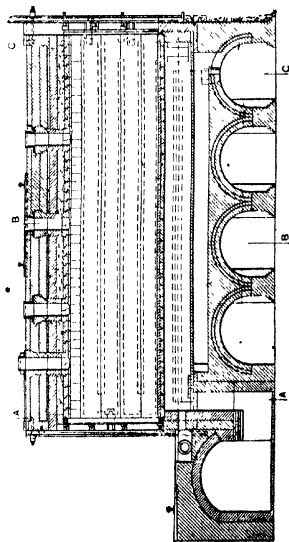Fig. 4.—Vertical-flued Coke Oven: the Otto-Hilgenstock, Non-Regenerative.

Fig. 5a.—Section through Semet-Solvay Oven.

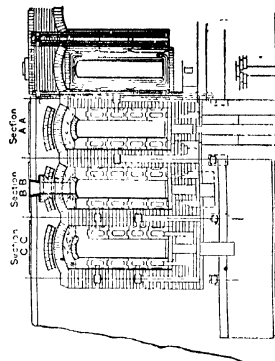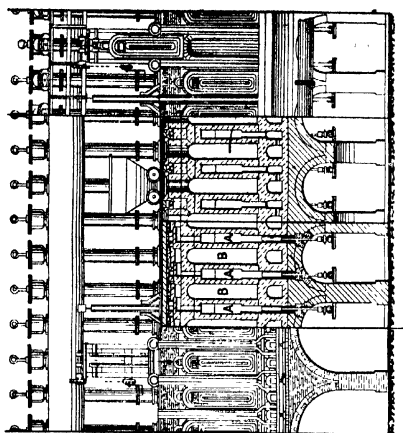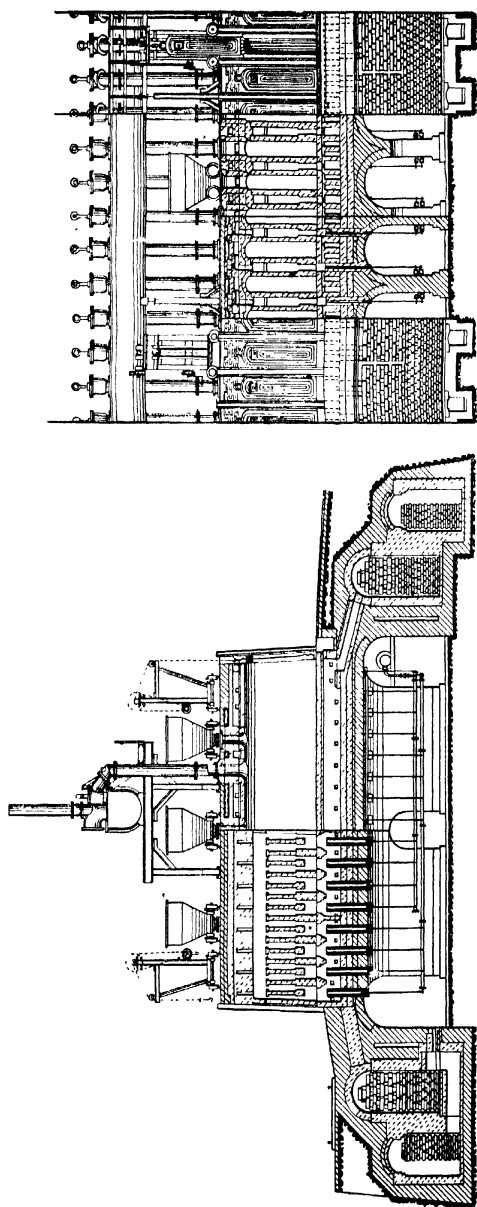Fig. 5.—Horizontal-flued Coke Oven: the Semet-Solvay, Non-Regenerative.

FIG. 6.—REGENERATIVE VERTICAL-FLUED COKE OVEN: THE OTTO-HILGENSTOCK

steam or electrically driven), a Root's blower, or some form of aspirator, through coolers. These coolers are either plain pipes or cylinders offering a large amount of atmospheric cooling surface, or are water-cooled chambers; in these condensers, the bulk of the remaining tar, together with the greater proportion of the ammonia liquor, is precipitated. From the condensers, the gases pass into the exhauster or aspirator, which then delivers them at a pressure into a tar-fog extractor. This vessel is employed to remove the last traces of tar which exist in the gas in an extremely fine

state of division, and which no amount of cooling would remove. The tar extractor, of which the Pelouze Andouin and Livesay are types, operates by dividing the gas into numerous thin streams by means of very small gas passages, the agglomeration and removal of the tar particles being effected by the wire drawing and friction thus afforded.

From the tar catcher the gases pass into the ammonia scrubber, where the last of the ammonia not recovered by the condensers is removed by contact with weak ammonia liquor and water. The types of ammonia scrubber generally em-
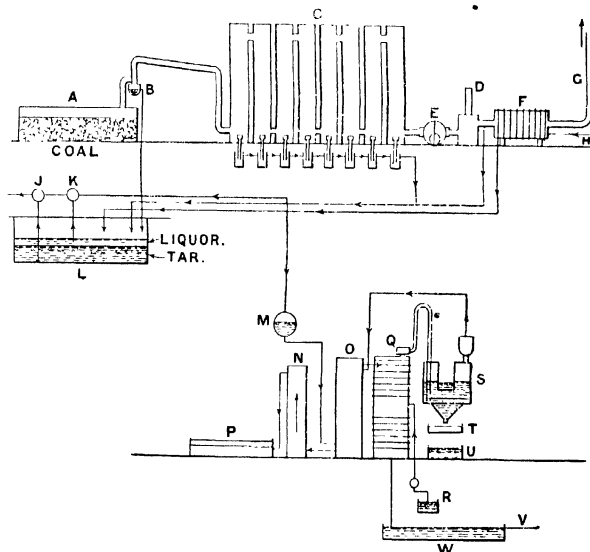

Fig. 7.—Showing Arrangement of Gas Cooling, Scrubbing of Sulphate of Ammonia Plant, Old Method.

A, Oven.	H, Liquor feed to scrubber.	N, Cooler for sulphate plant	R, Lime feed to still.
B, Hydraulic main.	J, Tar pump to store.	waste gases.	S, Saturator
C, Condensers or coolers.	K, Liquor pump to sulphate	O, Superheater.	T, Sulphate draining table.
D, Tar catcher (Pelouze).	plant.	P, Purifiers for sulphate	U, Mother liquor well.
E, Exhauster.	L, Tar and ammonia-liquor	plant waste gases.	V, Spent liquor outlet.
F, Scrubber.	tank.	Q, Ammonia still.	W, Spent liquor settling
G, Return main to ovens.	M, Liquor feed to still.		tank.

ployed are similar to those employed at gas works, and are either of the tower or rotary form. In the tower scrubber, the gases pass upwards through a mass of coke or other open material, meeting a downward current of water or ammonia liquor pumped in at the top. In the rotary scrubber, the gas is caused to impinge on revolving brushes or circular wooden screens, which dip into the water or liquor in the lower half of the vessel, and pass upwards with wet surfaces into the upper half of the scrubber, where the gas is circulating, and solution of ammonia is attained. The gas then passes forward to the benzol scrubber, which is constructed on similar lines to that employed for ammonia removal, creosote or anthracene

heavy oil being employed for the solution and recovery of the benzol vapour.

The gas having been freed from its tar, ammonia liquor, and benzol, is then passed forward to the ovens, where it is fed into the heating flues, the surplus being passed forward to boilers, gas engines, or gas holder.

The tars and ammonia liquors made in the hydraulic main, condensers, tar catchers, and ammonia scrubber are collected and run into separators or tanks, where the denser tar settles to the bottom, is withdrawn and despatched to the tar stores. The liquor which remain above the tar are run off to the sulphate of ammonia plant, where the liquor is pumped into overhead store tanks, whence it is allowed
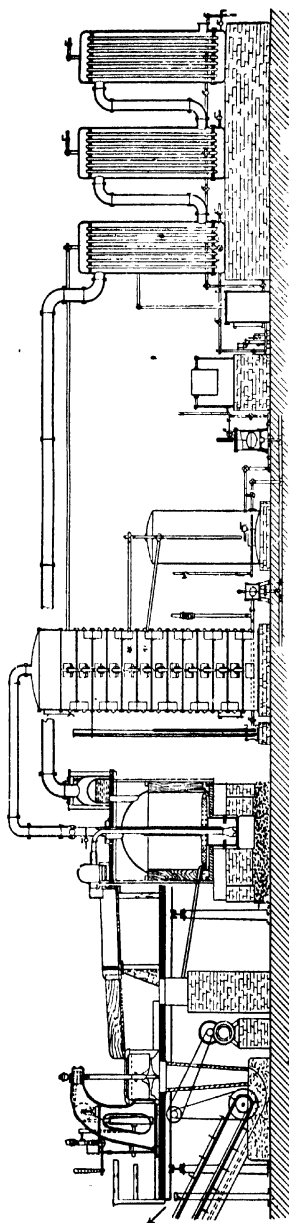
FIG. 8.—SULPHATE OF AMMONIA PLANT.

to flow by gravity through a preheater (heated by the waste gases from the sulphate plant), and thence into a distilling column, where it flows downwards, meeting in its travel an upward current of steam, which liberates the free or combined ammonia. In the lower half of the still, milk of lime is mixed with the liquor for the liberation of the ammonia from the fixed salts; the whole of the ammonia, together with steam, sulphuretted hydrogen, carbonic acid, and hydrocyanic acid, pass upwards through the still and into a lead-lined vessel called the saturator, containing sulphuric acid. The ammonia combines with the acid to form ammonium sulphate, which, when the liquor in the bath becomes saturated, crystallises out and is removed either by copper scoops, a valve, or by a steam injector. The sulphuretted hydrogen and other gases pass from the saturator to the preheater, where they serve to heat the liquor passing to the still; thence the gases travel to a condenser where they are cooled, and afterwards to purifiers where the sulphuretted hydrogen is removed by oxide of iron. The waste liquors, which should not contain more than 0·01 p.c ammonia, are run into the sewers or watercourses, and are a frequent source of trouble to the river boards. By the Otto-Hilgenstock method of by-product recovery, to be described later, the production of these waste liquors is entirely obviated.

The recovery of crude benzol from its solution in creosote or anthracene oil is effected in a distilling column somewhat similar to that employed for the recovery of ammonia from liquor, the heating of the solution of benzol in the absorbent being effected by wet steam assisted by dry steam. The vapours, steam, and benzol pass from the top of the still to a water-cooled coil, where they are together condensed, the condensates being separated by reason of their different densities. The grade of crude benzol thus obtained varies with the class of absorbent oil employed; with creosote, 62 p.c. of the product distils at 120°, with anthracene oil the benzol is richer, 80 p.c. distilling at 120°. For the rectification of crude benzol, the product is washed successively with strongest oil of vitriol, water, and caustic soda, and redistilled.

Direct Recovery Systems.—Two successful attempts have been made to simplify the old system of treatment of coke-oven gases for the recovery of ammonia, viz. the inventions of the Koppers and Otto-Hilgenstock Coke Oven Companies. Koppers treats his gases by the old system up to the point of the tar-fog extraction. He then reheats his tar-free gas by passing it in pipes surrounded by the hot gases coming from the ovens in an apparatus called a heat exchanger, and then passes the heated gas direct into a sulphate saturator, into which is likewise passed the ammonia from the liquor made in the condensers, which is distilled in an ordinary ammonia still. In short, Koppers abolishes the usual ammonia scrubber and substitutes the sulphate saturator, thus making his sulphate direct on the gas main (Fig. 9). By thus using the sulphuric acid in the saturator for scrubbing out the ammonia, Koppers dispenses with the water utilised in the old scrubber, thereby reducing the total amount of liquor produced, and

effecting an economy in the amount of steam required in the ammonia distillation.

A more extensive simplification is effected by the invention of the Otto-Hilgenstock Co. of Dahlhausen, who dispense entirely with the old condensing plant and remove the tar from the gases by means of a tar spray at a temperature above the dew-point of the liquors.. The tar-free gases then pass direct into a saturator, where the whole of the ammonia is caught by sulphuric acid. The gases issuing from the saturator still contain their liquors in steam
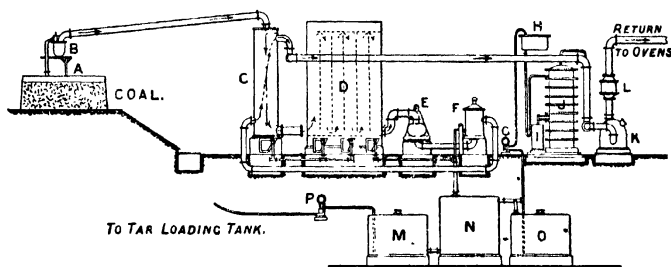

FIG. 9.—KOPPERS' BY-PRODUCT RECOVERY PROCESS.

A, Oven.
B, Hydraulic main.
C, Heat exchanger.
D, Condensers.
E, Exhauster

F, Tar extractor.
G, Liquor pump to still.
H, Feed tank to still.
I, Liming chamber.

J, Ammonia still.
K, Saturator.
L, Acid spray catch-box.
M, Tar store tank.

N, Tar of liquor receiving
      tank.
O, Liquor tank.
P, Pump delivering tar to
      railway trucks.

form, and the whole passes forward to the oven-flues, and the offensive and troublesome waste liquors are thus got rid of. The Otto system, by abolishing the condensing plant, liquor tanks, ammonia stills, lime mixers, and pumps, waste liquor tanks, &c., effects a great economy in ground space. It likewise saves nearly the whole of the steam required to distil the ammonia liquor made by the old condensing process, and, by passing the whole of the ammonia through sulphuric acid, losses of ammonia, which are liable to occur in the old process of ammonia liquor distillation, are rendered impossible. The ammonium sulphate made by the Otto direct-recovery, tests from 25 to 25·5 p.c. of ammonia, and contains only the merest traces of tar, viz. 0·05–0·1 p.c. (Figs. 10, 11, and 12).
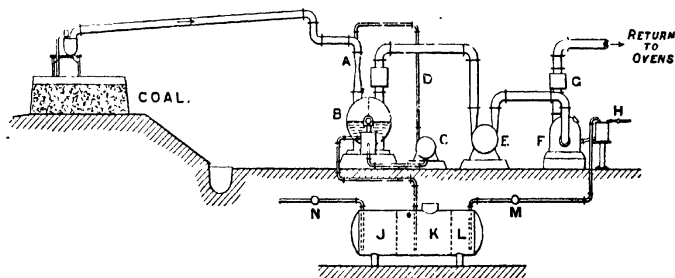

FIG. 10.—OTTO HILGENSTOCK BY-PRODUCT RECOVERY PROCESS.

A, Tar-spray.
B, Tar-spray receiving tank.
C, Tar-spray pump.
D, Tar-spray feed pump.
E, Exhauster.

F, Saturator.
G, Acid spray catch-box.
H, Mother liquor return
      pipe.

J, Tar store.
K, Tar spray overflow
      tank.
L, Condensing tank.

M, Pump delivering con-
      densings to saturator.
N, Pump delivering tar to
      railway trucks.

MODERN METHODS FOR THE RECOVERY OF
NAPHTHALENE AND BENZOLS.

Recovery of Naphthalene.—The gas from the saturator, which is now freed from both ammonia and tar, but still containing the benzol, moisture and naphthalene, passes through a lead-lined catch pot (not shown in the diagram, but whose situation prevents all fear of any acid spray being carried over from the saturator) and on to the naphthalene extractor and spray cooling tower, H. (Fig. 13.) This tower is quite devoid of any filling or apparatus, but at the top there are several jets through which cold water is sprayed at high pressure. The action of this mass of
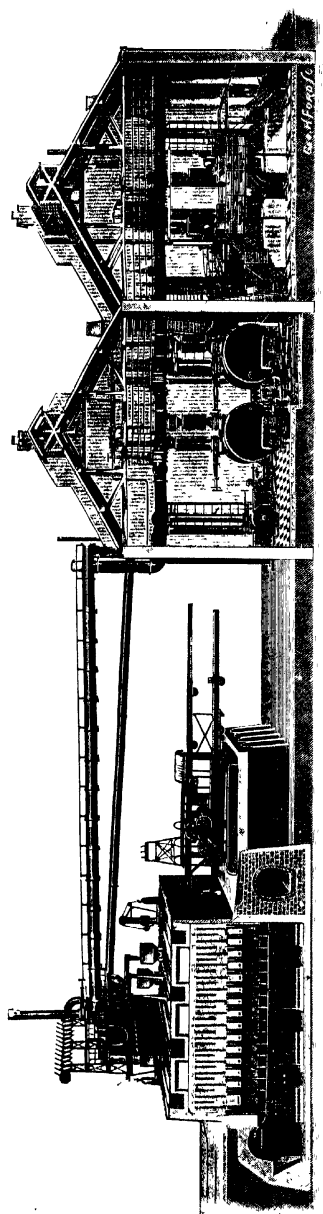
finely-divided cold water beating suddenly on to the hot gas produces a rapid chill, which, together with the concussion brought about by the water, precipitates and washes out practically all the naphthalene, which flows away along with the water into a catch tank beneath this apparatus. The naphthalene is filtered off whilst the water can be either allowed to flow away, or re-cooled and used over again continuously, as circumstances permit. This tower also serves the purposes of cooling the gases. It is necessary to extract the naphthalene, otherwise it would pass on to the benzol scrubbers, where it would be dissolved by the benzol wash oil, which would very soon become saturated with naphthalene and rendered useless for the purpose of collecting benzol The naphthalene thus extracted is of a pale yellow colour, and is readily sold in this country for 50s. a ton, which more than pays the cost of running this part of the plant

Recovery of Benzols.—The gas now being cooled but still containing the benzol, passes through the exhauster, K, and a second water cooler, L, and thence to the benzol scrubbers, MM, which vary in number according to the size of the plant (Fig. 13). These scrubbers are from about 50 to 70 feet high, the lower portion forming a reservoir for the circulating benzol wash oil, and the remaining portion being filled with wooden grids. Benzol wash oil is constantly circulated downwards over these grids, the gas having to pass upwards through them. By this means the gas is brought into very intimate contact with the oil, with the resulting absorption of the benzol After leaving these scrubbers the gas passes either wholly back to the ovens, or in the case of regenerative ovens. about one-half of it returns to the ovens, and the other half is used either for firing boilers, town lighting, operating gas engines, or any other purpose.

A fuller account of the process is given in a paper by Mr. E. Bury before the Institution of Mining Engineers in the year 1914, from which the following temperatures of a plant at New Brancepeth Colliery (Co. Durham) are taken :—

				Cent.
Hydraulic main	.	.	.	225°
Before tar extraction	.	.	.	86°
After ,, ,,	.	.	.	58°
In saturator	.	.	.	67°
After ,,	.	.	.	58°
After exhauster	.	.	.	66°

Distillation and Rectification of Benzols.— The ' wash oil ' containing the benzols in solution is sent on to the continuous crude benzol still, N (Fig. 14), where, after being pre-heated by the hot vapours coming away from the still, it passes downwards over a series of trays. Dry steam at about 100 lbs. pressure, reduced, however, at the still to 10 lbs. pressure, is delivered into the bottom of the apparatus, and passing upwards bubbles through the wash oil liberating the benzol hydrocarbons which it carries over into the condenser, P. Here the steam and benzols are condensed, and the condensed water and oil separated. The crude benzol then either passes into a storage tank, or (if its rectification is to be carried out) into the ' primary rectifying still,' s. The debenzolised

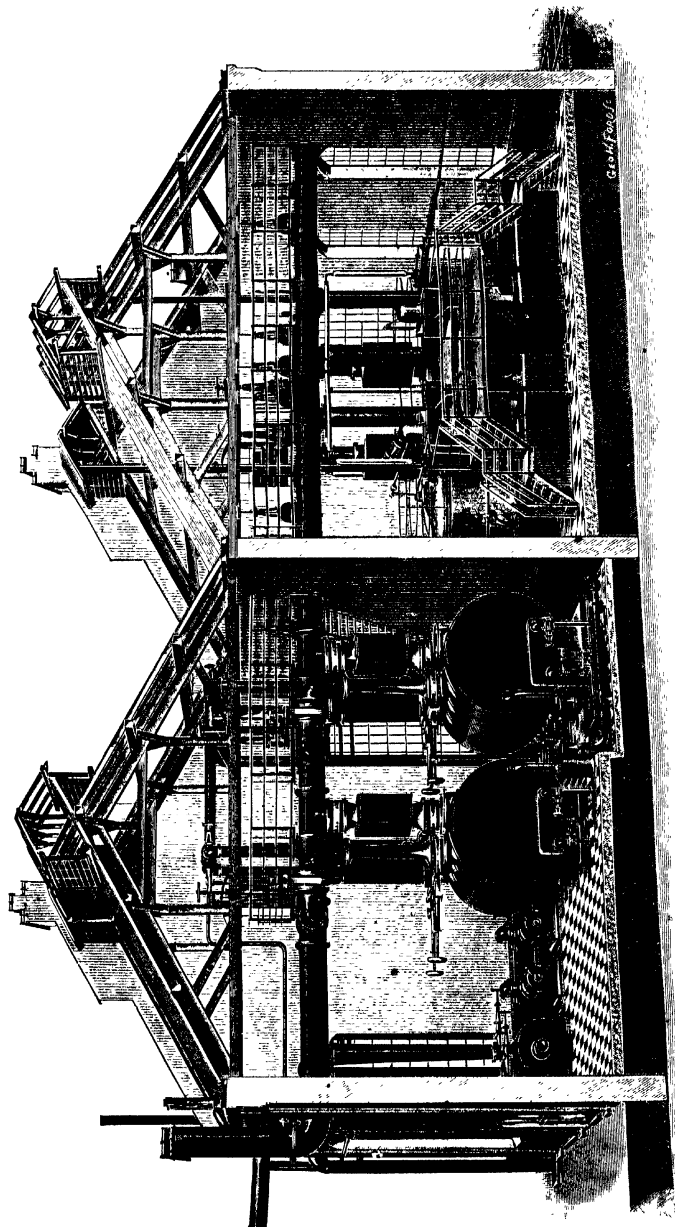FIG. 11.—MODEL OF OTTO HILGENSTOCK SYSTEM : PLANT ERECTED FOR THE SKINNINGROVE IRON CO

FIG. 12.—OTTO-HILGENSTOCK DIRECT RECOVERY PLANT ERECTED FOR THE SKINNINGROVE IRON CO

'wash oil' leaving the crude benzol still is passed through the refrigerator, R, whence, after being cooled down to the atmospheric temperature, it is sent into the 'oil storage tank,' T, and from there it is used over again in the benzol scrubbers.

The crude benzol is first of all fractionally distilled in the primary rectifying still, S, 3000–5000 gallons capacity and intermittent in its working, in which it is heated under high pressure by means of steam coils, and, with the aid of a long dephlegmating column, it is separated into :—

 (1) Crude 90 p.c. Benzol
 (2) ,, 90 ,, Toluol
 (3) ,, 90 ,, Xylol
 (4) ,, 90 ,, Solvent naphtha

Each of these fractions is separately condensed and pumped into a large vessel, v, termed the agitator, where it is successively treated with (a) pure strong sulphuric acid, and (b) a solution of caustic soda, in order to remove all resinous, basic, or acidic substances. Each of the 'washed' fractions is finally refractionated under reduced pressure in the 'secondary rectifying still,' W, and the redistilled resulting fractions, after condensation, are sent forward into their respective storage tanks, XYZ, ready for transport.

Other firms (e g the Simon-Carvés and the Simplex Companies) have also adopted efficient 'direct recovery' processes, on much the same lines as the Otto process just described, the chief difference between them being in the precise mechanical arrangement for the removal of tar and tar fog from the hot gas before it enters the saturator where the ammonia is absorbed.[1]
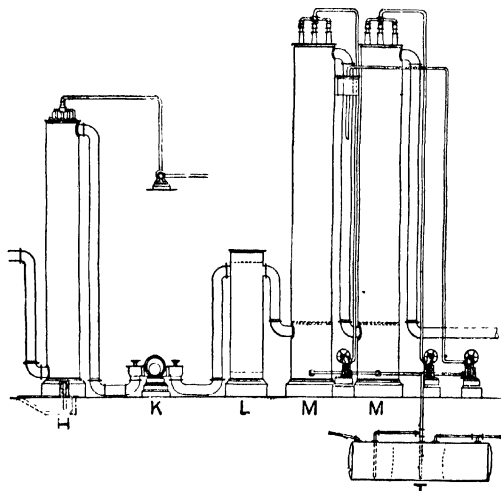
Alcohol from Coke Oven Gas.—Attention

Fig 13.—Otto Direct Recovery Process. (Benzol Recovers.)

should here be drawn to the successful process worked out by E. Bury and O. Ollander at the Skinningrove Ironworks for the absorption of the ethylene in coke oven gas by conc. H_2SO_4 (forming ethyl hydrogen sulphate), and its subsequent recovery therefrom as ethyl alcohol. The process, which is fully described in the Coal and Iron Trades Review for December, 1919 (q.v.), consists essentially in (a) absorbing the C_2H_4 from the dried, debenzolised, and H_2S-free gas by means of 95 p c H_2SO_4 in a series of towers, on the counter-current principle, at a temperature between 60° and 80°C. ; and subsequently (b) treating the strong acid containing the ethyl hydrogen sulphate with a current of steam in a special form of distilling column, so as to dilute it to between 70 and 75 p.c. strength, thereby also hydrolysing the ethyl hydrogen sulphate and liberating the resultant ethyl alcohol, which then distils over, and is condensed. The whole process is worked in a continuous cycle, the diluted acid being (c) reconcentrated to 95 p.c. strength in a Guillard 'concentration tower,' and then being reused for extracting ethylene from the gas. A notable feature of the process is that the small amount of SO_2 formed by the reducing action of the gas upon the hot conc. H_2SO_4 in the absorption towers is subsequently utilised to remove H_2S from the gas by the well-known reaction $2H_2S + SO_2 = 2H_2O + 3S$, so that all the S contained as H_2S in the gas is removed and recovered from it without the employment of elaborate 'iron-oxide' or other purifiers. From the gas (containing between 1·75 and 2·25 p.c. ethylene) evolved in carbonising a typical Durham coking coal in regenerative ovens, with the 'direct'

[1] See a paper on Recent Developments in By-product Coking, by Mr. G. Blake Walker. (Proc. Inst. Civil Engineers, 1917.)
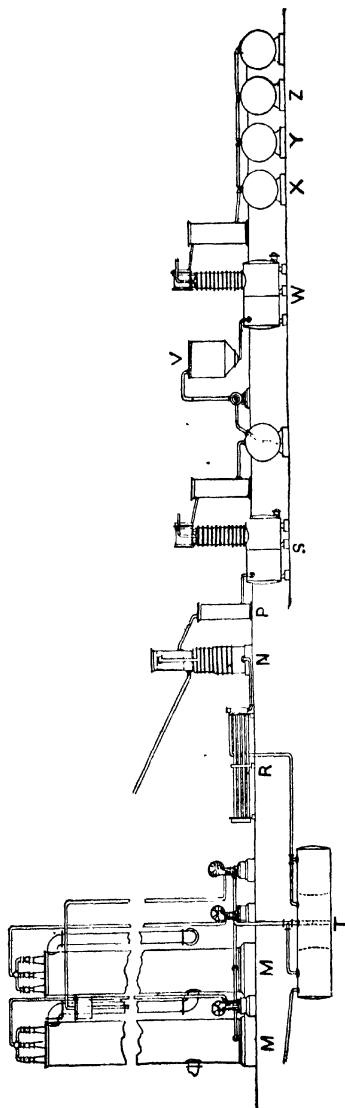
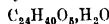FIG. 14.—OTTO DIRECT RECOVERY PROCESS. (Benzol Rectification.)

system of recovering tars, naphthalene, ammonia, and benzol, it is claimed to be possible to obtain about 1·5 gallons of 95 p.c. ethyl alcohol per ton of coal at a present-day cost not exceeding one shilling per gallon.

Utilisation of Coke-Oven Gas.—The composi-tion of the surplus gas obtained in working the process depends somewhat on whether it is ' debenzolised ' or not, as well as on the character of the coal carbonised ; but for gas from a typical Durham coking coal it would be approxi-mately as follows :—

							Gross calorific value B.Th.U. per cub. ft. at 15°C. and 760 mm.
	CO_2	CO	C_nH_m	CH_4	H_2	N_2	
(1) Without benzol recovery	2·5	6·5	3·2	28·0	48·0	11·8	536
(2) ' Debenzo-lised '	2·5	6·5	2·0	25·0	55·0	9·5	485

With a regenerative oven giving 5000 cubic feet of such surplus ' debenzolised ' gas per ton of coal carbonised, the corresponding heat units available for outside purposes would be 2,450,000 (*gross*) and 2,150,000 (*net*) B.Th.Us. respectively. This gas may be utilised (*a*) for generating steam in a Bonecourt surface-com-bustion boiler with an efficiency of 92 p.c. ; or (*b*) for generating power in internal combustion engines with an efficiency of from 20 to 25 p.c. Where coke-ovens are erected in conjunction with blast-furnaces and steel-works, the surplus gas is usually mixed with cleaned blast-furnace gas, and the mixture used both for generating power in gas-engines and also for heating purposes in open-hearth steel-furnaces, soaking pits, &c. In both Germany and America, coke-oven gas (after purification in the usual manner from H_2S and cyanogen compounds) is exten-sively used as a public supply for domestic purposes. As long ago as 1910, Parliament granted powers for the supply of gas from Lord Ellesmere's Brackley Coke-Works to the urban district of Little Hulton (Lancs.), under a guarantee of a minimum illuminating power of 14 candles when tested in a No. 2 Metropolitan Argand burner, and a gross calorific value of 550 B.Th.U. per cubic foot at 60°F. and 30 mm. pressure. Its average composition was $CO_2=2·5$, $CO=7·0$, $C_nH_m=3·8$, $CH_4=31·0$, $H_2=49·0$, and $N_2=6·7$ p.c. More recently, the town of Middlesbrough now draws its entire gas supply from a battery of Otto regenerative ovens at the Newport Ironworks. Also Leeds takes part of its supply from the Simon-Carvès ovens of the Middleton Estate and Colliery Co., Ltd. ; whilst at the Birmingham (Saltley) Gasworks a battery of 66 Kopper's regenerative ovens, fired by Mond gas, has been installed for the production of furnace coke and town's gas.

Literature—W. A. Bone, Coal and its Scientific Uses, chap. xvi. 1918 ; and G. Stanley Cooper, By-Product Coking, 1917 ; Report of Coal Conservation Committee, 1918, pp. 79–81. W. A. B. and E. B.

COLALIN. Syn. for cholalic acid

$$C_{24}H_{40}O_5,H_2O$$

COLATANNIN *v.* TANNINS.

°COLCHICEÏNE *v.* COLCHICUM.

COLCHICUM. *Meadow saffron.* (*Colchique,* Fr. ; *Herbstzeitlose,* Ger.) *Colchicum autumnale* (Linn.) ; the corms and the seeds are official in the B.P. and U.S.P., the alkaloid colchicinn only in the U.S.P. The plant is found in meadows and pastures throughout Europe, where its crocus-like flowers, usually of a lilac hue, occur in September and October.

The only constituent of importance is the alkaloid *colchicine* $C_{22}H_{25}O_6N$, which was regarded as identical with veratrine by Pelletier and Caventou as early as 1820, and was recognised as a separate individual by Geiger and Hesse (Annalen, 1833, 7, 274). Its constitution has in part been elucidated, chiefly by Zeisel (Monatsh. 1883, 4, 162 ; 1886, 7, 557 ; 1888, 9, 1 ; Zeisel and Johanny, *ibid.* 1888, 9, 865 ; Zeisel and Stockert, *ibid.* 1913, 34, 1327, 1339), and more recently by Windaus (Chem. Soc. Abstr. 1911, i. 904 ; 1915, i 708). According to these investigations the formula may be resolved into :—

$$\text{MeO}$$

$$\underset{\text{MeO}}{\overset{\text{MeO}}{\bigcirc}} \!\!- C_{10}H_8O(OMe)NH \cdot CO \cdot CH_3$$
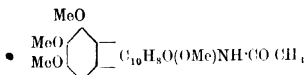
By boiling with 0·2 p c sulphuric acid one methoxy group is hydrolysed and there results *colchiceine* $C_{21}H_{23}O_6N,\frac{1}{2}H_2O$, crystals, m.p. 139°, or anhydrous, m.p 172°, which has been described, probably erroneously, as a constituent of the plant. Zeisel regards colchiceine as a carboxylic acid ; Windaus, on account of the green colouration by ferric chloride, considers it an enol. By methylation it is transformed back to colchicine, and to N-methylcolchicine. Concentrated hydrochloric acid hydrolyses colchicine further, removing the N-acetyl group and finally the remaining three methyl groups, yielding *colchicinic acid* $C_{16}H_{11}NO(OH)_4 \cdot OH$. Windaus obtained, by permanganate oxidation of colchicine, 3 : 4 . 5-trimethoxy-*o*-phthalic and succinic acids, and by potash fusion of colchicine acid terephthalic and trimellitic (1 : 2 : 4-benzenetricarboxylic) acids, which indicates that the complex $C_{10}H_8$ of the above formula contains a (second) benzene ring. Iodine and sodium hydroxide remove one carbon atom, oxidising to $C_{20}H_{22}O_5NI$, which may be reduced to a substance $C_{20}H_{21}O_5N$ Colchicine apparently contains no heterocyclic nitrogen. According to D. R. P. 279999 of Hoffmann-La Roche and Co. tetrahydrocolchicine is formed by reduction with hydrogen and palladium ; this base is amorphous and less toxic than the parent alkaloid.

Properties.—Pure dry colchicine usually forms a yellowish varnish, softening at 142°, and wholly melting at 147° ; but Clewer, Green, and Tutin (Chem. Soc. Trans. 1915, 107, 839) obtained from ethyl acetate soft, pale yellow needles, m.p. 155°–157° ; $[\alpha]_D-121°$ (0·88 gram per 100 c.c.) in chloroform, $-429°$ in water. Zeisel first crystallised it from chloroform, with two molecules of chloroform of crystallisation ; according to Merck (Apoth. Zeit. 1916, 31, 399), there are two such compounds, $B,CHCl_3$ and $2B,CHCl_3$. The crystalline colchicine of commerce is the chloroform compound, in which the 14–16 p.c. of chloroform is retained tenaciously, and is only given off slowly at 100°. According to Merck, pure colchicine, dissolved in 3 parts of water, slowly crystallises as the hydrate $B_2,3H_2O$. Colchicine has a very bitter taste. It dissolves slowly but abundantly in water, readily in alcohol, chloroform, and hot benzene, hardly at all in ether. Being an acid amide, it is a very feeble base,

and one of the few alkaloids which can be extracted from acid solution by chloroform. Its salts are generally hydrolysed by water ; the only crystalline one appears to be the aurichloride $B,HAuCl_4$, m.p. 209°. Dilute mineral acids and alkalis colour colchicine solutions intense yellow. Nitric acid (d. 1·4) colours the solid alkaloid a deep violet, changing to yellow, and finally to green (characteristic). Tannic acid, phosphomolybdic acid, potassium triiodide, and bismuth potassium iodide are the most sensitive precipitants ; potassium mercuric iodide only precipitates in acid solution.

Extraction, Toxicological Recognition, Assay.—These are all based on the removal from acid solution by chloroform. To prepare colchicine, uncrushed seeds are exhausted with 85–90 p.c. alcohol. The extract is evaporated and diluted with much water, filtered from fat, and extracted with chloroform. The chloroform solution is evaporated to the consistency of olive oil and diluted warm with small quantities of alcohol, until the whitish masses which separate at first again dissolve After cooling to 0° for some time yellow needles of the chloroform compound separate, which may be suspended in very little hot water and decomposed by steam. The aqueous solution is then evaporated *in vacuo*. On a smaller scale, *e.g.* in the toxicological recognition, the acid solution is first agitated with petrol and then with chloroform. The residue, after evaporation of the latter solvent, is dissolved in water, and precipitated with tannic acid. The precipitate is decomposed with lead oxide and extracted with alcohol or chloroform. On evaporation the solid product so purified can be tested by the reactions given above ; $\frac{1}{2}$ m g. will give the nitric acid test (*see* also Allen's Commercial Organic Analysis, 1913, vol. vii. pp. 4–12).

The assay of colchicum seeds and the estimation of colchicine is based on weighing the residue from a chloroform extract of an acid solution. previously washed with petrol (Farr and Wright, Pharm. J. 1891, [iii] 21, 957 ; for the assay of corms, *v.* Lyons, *ibid.* 1909. [iv.] 28, 270 ; *v.* also the more complicated process of the U.S.P.).

The alkaloidal content of the seeds and corms varies greatly, mostly from 0·2 to 0·8 p.c. in the seeds, from 0·1 to 0·5 p.c. in the corms. The Brussels Conference agreed that the seeds only should be used. The alkaloid occurs to a slight extent also in the flowers. It is present in other species of the same genus, and also in the large tubers of *Gloriosa superba*, L. (N.O. *Liliaceæ*), common in India and Ceylon (Clewer, Green, and Tutin, *l.c.*, found 0·3 p.c. of dry weight). Perhaps this plant would afford a suitable commercial source of colchicine. Colchicum is a specific in acute gout, and an ingredient of many advertised gout remedies. It is a gastro-intestinal irritant, and may cause vomiting and purging. Its degradation and substitution products are much less active or without action (Führner, Arch. exp. Path. Pharm. 1913, 72, 228).　　　G. B.

COLCOTHAR. The reddish-brown residue of ferric oxide formerly obtained in the manufacture of fuming oil of vitriol from iron sulphate.

COLEMANITE. A hydrated calcium borate $Ca_2B_6O_{11},5H_2O$, containing 50·9 p.c. boron

trioxide. It is found in California at Death Valley in Inyo Co., and the Calico district in San Bernardino Co.; and although not discovered until 1882 and 1883, is now of some importance as a material for the preparation of borax and boracic acid. Cavities in the massive, white material are lined with beautiful, water-clear crystals with a profusion of brilliant facets; these are monoclinic, with a perfect, pearly cleavage parallel to the plane of symmetry. They are considerably harder (H. 4–4½) than borax; sp.gr. 2·42. The mineral forms, together with other borates and borosilicates, a bed 7 to 10 feet in thickness in sandstones and clays.

The compact minerals, *priceite* from Oregon and *pandermite* from Asia Minor, have very nearly the same composition ($Ca_5B_{12}O_{23},9H_2O$), and they have been regarded as impure, massive varieties of colemanite. E. S. Larsen (1917) has, however, by an examination of the optical characters established the identity of priceite and pandermite, and proved them to be triclinic and distinct from colemanite. These also are mined as borates *v* BORON.   L. J. S.

COLLIDINE *v.* BONE OIL.

COLLIN. A preparation made by heating a solution of hide powder or gelatin with caustic soda and neutralising with acetic acid. Used in the analysis of tannin and tanning materials (Parker and Payne, J. Soc Chem. Ind. 1904, 648; Wood and Trotman, *ibid.* 1904, 1071).

COLLODION *v.* PHOTOGRAPHY.

COLLODION COTTON *v.* EXPLOSIVES.

COLLOIDS. In 1861 Graham pointed out that substances which crystallise readily from water are characterised by a high power of diffusion and by the ability to pass through animal or vegetable membranes; substances, on the other hand, which cannot easily be obtained in the crystallised condition are characterised by a low power of diffusion and by inability to pass through animal or vegetable membranes. Graham termed substances of the first class, such as sucrose or sodium chloride, *crystalloids*; and those of the second class, such as starch, gum, or albumin, *colloids*. The separation of a colloid from a crystalloid is effected by dialysis, a process based on the inability of a colloid to pass through parchment or other membrane.

At the present time, the term 'colloid' is used in a sense different from that in which Graham employed it, and is to be interpreted as referring, not so much to a particular class of substances, as to a condition which very many, if not all, chemical elements or compounds may be made to assume. From the modern standpoint 'colloidal solutions' are to be regarded as forming a special group of the physical systems built up from two substances, one of which is present in relatively small quantity. Such systems may be described as 'dispersed systems,' the substance present in excess being termed the 'dispersion medium,' and the other the 'dispersed phase.' The main groups of dispersed systems are: (1) mechanical suspensions; (2) colloidal solutions; (3) molecular solutions, the feature which characterises each group being the degree of dispersion or division of the dispersed phase. From this point of view a colloid solution is a dispersed system in which the degree of dispersion is intermediate between that of a mechanical suspension and that of a molecular solution.

Now the smallest suspended particle which can be observed directly under the microscope is of the order $0·1\mu$, and this size of particle may be taken as roughly marking the boundary between mechanical suspensions and colloidal solutions. On the other hand, the size of an average molecule is $0·0001\mu–0·001\mu$, and although there is no hard-and-fast line of demarcation to be drawn between the three groups of dispersed systems, the dispersed phase of a colloidal solution may conveniently be regarded as consisting of particles of the dimension $0·1\mu–0·001\mu$. This conception of the continuity of dispersed systems, from mechanical suspensions at one extreme to molecular solutions at the other, finds its justification in the graded character of the physical properties of the three groups, as evidenced, for example, by observations on diffusion and filtration, and by osmotic, optical, and electrical experiments (*see* below). It should further be observed that the colloid condition is independent, not only of the chemical character of dispersion medium and dispersed phase, but also of their states of aggregation. Thus, whilst in many colloidal solutions, such as those of platinum, arsenious sulphide or ferric hydroxide, the dispersion medium is a liquid, and the dispersed phase is a solid, there are other cases, as, for example, an aqueous solution of gelatin, in which the dispersed phase also is a liquid. The terms 'suspension colloid' and 'emulsion colloid' are commonly used to differentiate the two cases. Again, there appear to be many cases in which both the dispersion medium and the dispersed phase are solids, instances of this kind being furnished by ruby glass, some coloured minerals, and probably also alloys in certain conditions.

Osmotic properties of colloidal solutions.— The osmotic pressure of a colloidal solution is extremely low. According to Duclaux, for instance, the osmotic pressure of an 8·86 p.c. ferric hydroxide solution is only 22·6 cm. of water, which is about equal to the pressure given by a solution of sucrose containing one-thirtieth of a gram in 100 grams of water. It has, indeed, been suggested that the osmotic pressures which have been observed for colloidal solutions are due, not to the colloids themselves, but to small quantities of electrolytes associated with the colloids. While it is certainly true that the removal of the last traces of electrolytes from a colloidal solution is no easy matter, and that electrolytes are extremely active material from the osmotic point of view, still the most recent investigations indicate that colloidal solutions do possess a definite, if small, osmotic pressure. In this connection the epoch-making work of Perrin is of great significance, for his determination of the Avogadro number, based on a study of the distribution of suspended gamboge particles in a vertical column, really involves the extension of the gas laws to mechanical suspensions. This extension is justified by the experimental results (*see* Perrin's book, Atoms) and it is therefore to be expected that the osmotic pressure of a colloidal solution will be related in the usual way to concentration and temperature.

It appears, however, that the osmotic pressure of a colloidal solution may not be in every case completely defined, as is that of a crystalloidal solution, by concentration and temperature. Thus Moore and Roaf have found (Biochem. J. 1906, 2, 34) that the osmotic pressure of a given gelatin solution at a given temperature depends, to some extent, on its previous history, while Lillie has found (Amer. J. Physiol. 1907, 20, 127 ; see also Bayliss, Proc. Roy. Soc. B, 1907, 81, 269) that the osmotic activity exhibited by the colloid itself is modified by the presence of electrolytes in a remarkable degree. The osmotic pressure of a colloidal solution, it is clear, will be determined not only by the total solute concentration and by the temperature, but also by the actual degree of dispersion.

The depression of the freezing-point and the elevation of the boiling-point of water by a dissolved substance are quantitatively related to the osmotic pressure of the solution, and, like the latter, may be made the basis for a determination of the molecular weight of the solute. The freezing-point and boiling-point of a colloidal solution are, however, very slightly different from those of water itself, and the experimental error of the determination of the molecular weight of the colloid by this method is relatively large. In view, further, of the fact that the osmotic activity of a colloid depends on other factors than those of concentration and temperature, it is obvious that the values for the molecular weight of a colloid deduced from its effect on the freezing-point or boiling-point of water have a very limited significance. Such values have reference only to the particular condition of the colloid at the time of the determination.

In connection with the interesting question of the osmotic activity of colloids, attention should be directed to the investigations of McBain and others on soap solutions (Chem. Soc. Trans. 1919, 115, 1279).

Colloids in an electric field.—In 1892 Linder and Picton observed (Chem. Soc. Trans. 1892, 61, 148) that when two wires, connected with the terminals of a battery, are placed in a colloidal solution of arsenious sulphide, this substance is attracted by the positive pole and is gradually transported thither. Ferric hydroxide in colloidal solution is, on the other hand, attracted by the negative pole. It appears, therefore, that the particles of colloidal arsenious sulphide carry a negative charge, whilst those of colloidal ferric hydroxide carry a positive charge. Other colloids are similarly found to carry a definite charge ; thus chromium and aluminium hydroxides, methylene blue, Bismarck brown and hæmoglobin, are electropositive ; tannin, caramel, starch, platinum, gold, and indigo are electronegative. Very significant in this connection is Hardy's observation (J. Physiol. 1899, 24, 288), that protein is electronegative in an alkaline medium, but electropositive in an acid medium. A reversal of the electric charge on a colloid has been observed in other cases also (*see* Burton, Phil. Mag. 1906, 12, 472). The behaviour of substances in colloidal solution, when exposed to the action of an electric force is very similar to the behaviour of suspensions in the same circumstances, for when wires connected with the terminals of a battery are immersed in suspensions of quartz powder, gum mastic, or shellac, the suspended particles move towards the positive pole.

Colloids and the ultramicroscope.—The view that there must be a close relationship between colloidal solutions, on the one hand, and mechanical suspensions on the other, is strongly supported by various other lines of evidence. Thus the majority of colloidal solutions exhibit the Tyndall phenomenon, *i.e.* the opalescence observed when a powerful beam of light is passed through a fluid medium containing definite suspended particles. Further, the ultramicroscope, devised by Zsigmondy and Siedentopf, makes it possible to detect the individual particles in colloidal solutions, even when the most powerful microscope fails to reveal any trace of heterogeneity.

There are, however, cases on record in which colloidal solutions, even when examined with the ultramicroscope, have been found free from distinct particles. On the other hand, evidence has been adduced (Lobry de Bruyn, Rec. trav. chim. 1904, 23, 155, 218) showing that solutions of a heavy crystalloid, such as sucrose, are non-homogeneous. Hence it is evidently impossible to draw a hard-and-fast line of division between colloidal and crystalloidal solutions, so far at least as the size of the particles of the dispersed phase is concerned.

The particles which are detected in a colloidal solution with the help of the ultramicroscope are seen to be in a state of constant motion—a phenomenon essentially the same as the Brownian movement exhibited by gamboge or fat particles suspended in water. The finer the particles the more rapid is their movement, and a study of the relationship between the size of the particle and its rate of movement has led to a calculation of the rate at which a particle of molecular size would move. The value so calculated is in good agreement with the value deduced from the kinetic theory, and this agreement is regarded as amounting to a definite proof of the kinetic nature of heat.

Separation of colloids from their solutions.—Substances in colloidal solution pass through the finest filter paper, but if the close relationship between mechanical suspensions and colloidal solutions is borne in mind, it will be seen that the question whether filtration can be effected in the latter case as in the former reduces itself to the question whether filters with sufficiently small pores can be procured. The most successful attempts that have been made to solve this problem depend on the impregnation of a suitable supporting medium with a colloid such as gelatin or collodion. Filter paper, for instance, may be soaked in gelatin solution and then hardened with formaldehyde, or impregnated with a solution of collodion in glacial acetic acid and then dipped in water. As the concentration of the impregnating gelatin solution is increased, the permeability of the filter to colloids diminishes, so that a series of graded filters can be prepared which may be employed to sort out a number of colloidal solutions, according to the size of the particles they contain (*see* Bechhold, Zeitsch. physikal. Chem. 1907, 60, 257). It is noteworthy that these ' ultra-filters,' as they are called, may be

employed to separate oil-water emulsions (*see* Hatschek, J. Soc. Chem. Ind. 1910, 29, 125).

Another method of separating a colloid from its solution is to precipitate the colloid and then filter off in the ordinary way. It is found that in relation to precipitating or coagulating agents, solutions of suspension colloids behave differently from solutions of emulsion colloids. The former give non-viscous solutions which are coagulated by small quantities of electrolytes; these colloids are known also as 'non-reversible,' for when once they have been separated they do not again pass into solution by mere contact with water; their solutions can be obtained only by indirect methods. Emulsion colloids, on the other hand, give viscous solutions which are not readily coagulated by electrolytes; they are also termed 'reversible' colloids, because, even if separated from solution by any means, they will again pass into solution on mere contact with water.

The coagulation of suspension colloids, such as arsenious sulphide or ferric hydroxide, is brought about by extremely small quantities of electrolytes. When experiments are made to determine the minimum concentration of various electrolytes required to precipitate colloidal arsenious sulphide, it is found that this minimum concentration is of the same order for all salts containing cations of equal valency; the higher the valency of the cation, the smaller is the concentration of the electrolyte required to bring about coagulation. In relation to colloidal ferric hydroxide, on the other hand, the coagulating power of a salt is mainly determined by the valency of the negative ion; the valency of the cation is relatively unimportant. The contrast in this respect between colloidal arsenious sulphide and colloidal ferric hydroxide is very interesting in view of the fact that the colloid particles of arsenious sulphide are negatively charged, while those of ferric hydroxide are positively charged. The full significance of this was first emphasised by Hardy (Zeitsch. physikal. Chem. 1900, 33, 385), who formulated the rule that the ion of an electrolyte which determines the coagulation of a colloidal solution is the one which has a charge opposite in sign to that on the colloid particles. The validity of this rule has been extensively confirmed.

The 'coagulum' or 'hydrogel' obtained when a solution of a suspension colloid is precipitated by a salt contains some of the acidic or basic part of the salt. Thus the coagulum obtained when colloidal arsenious-sulphide is precipitated with barium chloride, is found to contain barium, and in proportion as the coagulum retains barium, the filtrate becomes acid. The barium cannot be removed by continued washing with water, but may be replaced by an equivalent quantity of another metal by digesting the coagulum with a solution of the chloride of this metal.

If, as suggested by the facts just mentioned, the coagulation of a suspension colloid by a salt is essentially a neutralisation of electric charges, it may be expected that colloids of opposite electrical sign will precipitate each other. In harmony with this, it is found that while no coagulation occurs when colloidal solutions ('hydrosols') of the same electrical sign are mixed, precipitation immediately follows the

addition of the solution of a positive colloid to the solution of a negative colloid, unless one of the colloids is in very large excess. For a certain proportion of the colloids, the precipitation of both is complete, but as the quantities deviate from this optimal ratio, precipitation is increasingly incomplete. The precipitation of egg albumin by solutions of various complex acids—*e.g.* molybdic, tungstic, and tannic acids—furnishes an example of the mutual coagulation of two colloids. Metaphosphoric acid, too, forms a pseudo-solution or hydrosol which precipitates albumin, while the crystalloidal orthophosphoric acid has no such effect.

The separation of emulsion colloids, such as serum protein, from their solutions, may also be effected by the addition of electrolytes, but the process is essentially distinct from the corresponding precipitation of suspension colloids; it is not electrical in character. When a number of alkali salts are arranged according to their efficiency in precipitating emulsion colloids, the order is practically the same as when they are arranged according to their efficiency in salting out an organic compound from water or according to their power of lowering the solubility of gases in water. The precipitation of emulsion or reversible colloids by neutral alkali salts appears, therefore, to be closely allied to the process of 'salting out,' and this result of itself shows that solutions of reversible colloids approximate more closely to true solutions than do solutions of suspension colloids.

Not only are emulsion colloids themselves very slightly sensitive to electrolytes, but in presence of an emulsion colloid the precipitation of a suspension colloid by salts is more or less inhibited. This is not due to an increase in the viscosity of the medium and consequent increase of resistance to sedimentation, for the protective effect is exhibited by quantities of the reversible colloid insufficient to cause any appreciable change in viscosity. It is probable that the emulsion colloid forms a thin envelope round each particle of the suspension colloid and so prevents the aggregation and subsequent flocculation of the particles.

Adsorption.—Reference has already been made to a difference of electrical potential as determining in some cases the relation between a colloid and its environment. There is, however, another factor which must be taken into account in the consideration of this question, and that is the relatively enormous surface of contact between the colloid and the surrounding medium. The evidence sketched in the foregoing paragraphs shows that a colloidal solution is really a two-phase system, consisting of a dispersion medium in which are distinct suspended particles of extremely small size. Now, it is obvious that as a given quantity of matter is divided up more and more finely, its surface area increases regularly. The surface area, for instance, of a single sphere with a diameter of 1 mm. is 0·0314 sq. cm.; if the matter composing this sphere were broken up into a number of smaller spheres, each 0·0001 mm. in diameter, the total surface area of the spheres would be 314 sq. cm. It is evident, therefore, that in a colloidal solution with its fine suspended particles, there must be relatively a very large surface of contact between the colloid and its medium.

On the basis of the two-phase character of colloidal solutions and the large surface development of the colloid phase, the relation of colloids to each other and to various solid and dissolved substances may be regarded as being essentially of the nature of 'adsorption.' This term is used in reference to the observation that when a substance is introduced into a two-phase system, and provision is made for its distribution throughout the system, it is frequently found concentrated at the surface of one of the phases. The nature of this phenomenon will perhaps be best appreciated by contrasting it with cases in which the substance is distributed uniformly in each phase of the two-phase system. When iodine is shaken up with two immiscible liquids, such as water and carbon tetrachloride, a state of equilibrium is soon reached at which the concentration of the iodine is uniform throughout the aqueous phase; uniform also (but different) throughout the carbon tetrachloride phase. If c_1 is the concentration of iodine in the aqueous layer, and c_2 its concentration in the carbon tetrachloride layer, then c_2/c_1, the 'partition coefficient,' is found to be a constant, independent of the absolute values of c_1 and c_2. This is a rule applicable to the distribution of any substance between two immiscible liquids, provided the molecular condition of the substance is the same in each liquid If, on the other hand, the molecular weight of the substance in the first liquid is n times its molecular weight in the second liquid, then c_2^n/c_1 is a constant, independent of the absolute values of c_1 and c_2. If, conversely, the distribution of a substance between two liquids at various concentrations has been found to be such that c_2^n/c_1 is a constant, the conclusion may be drawn that the molecular weight of the substance in the first liquid is n times its molecular weight in the second liquid

The distribution of a substance in a two-phase system which consists, not of two immiscible liquids, but of a solid and a liquid, is generally quite different in character. When, for instance, acetic acid solutions of various concentrations are shaken up with carbon, in a state of equilibrium is rapidly attained, and it is found that some of the acetic acid has been taken up by the carbon. If c_s and c_l represent the equilibrium concentrations of the acetic acid in the solid and the liquid phase respectively, then the experiments show that $c_s^{2\cdot35}/c_l$ is a constant. According to the foregoing paragraph, this would mean, on the assumption of a uniform distribution of the acetic acid throughout the carbon, that the molecular weight of acetic acid in the carbon must be less than half what it is in water. This conclusion must obviously be rejected, and the assumption of a uniform distribution of the acetic acid throughout the carbon is incorrect. The acetic acid must be concentrated at the surface of the carbon, a view supported by the rapidity with which equilibrium is established. The acetic acid is said to be 'adsorbed' by the carbon, and the phenomenon is termed 'adsorption.'

The distribution of a substance in a two-phase system where one of the phases is a solid with largely developed surface, is generally found to consist in an adsorption equilibrium. This is indicated, qualitatively, by the concentration of the substance in the solid phase increasing more slowly than its concentration in the liquid phase, and quantitatively by the validity of the formula $c_s^n/c_l =$ constant. In this way it has been shown, to quote one or two examples, that the taking up of gases by charcoal, the removal of arsenious acid from solution by freshly precipitated ferric hydroxide, and the dyeing of silk with picric acid and numerous other colouring matters, are all cases of adsorption. The complexes formed, although not due to chemical combination in the strict sense, and although lacking the characteristics associated with a definite chemical substance, are frequently referred to as 'adsorption compounds.' As van Bemmelen especially has shown, colloids in the form of hydrogels have a very marked power of adsorbing other colloids, crystalloids and water, and evidence is accumulating in favour of the view that the behaviour of colloids in solution towards other substances is also to be interpreted in terms of adsorption.

The question may be asked Is there any physical reason for the concentration of a substance at the surface of one of the phases in a two-phase system, such as a colloidal solution undoubtedly is ? The answer is that if surface tension considerations only are taken into account, then it follows on thermodynamical grounds that the most stable relation between the two phases of a colloidal solution is the one characterised by a minimum surface tension. Hence if the substance present in the solution lowers the surface tension of the solvent, that substance will accumulate in the surface layer of the solution. That such spontaneous accumulations may occur in the surface layers of solutions has been shown by Ramsden (Proc. Roy. Soc. A, 1903, 72, 156), who observed the formation of solid or highly viscous coatings on the free surfaces of protein and many other colloidal solutions.

Bearing of colloid chemistry on technical problems.—The rôle played by colloids in the operations of applied chemistry is of great importance. In the manufacture of starch, cellulose, glue, leather, caoutchouc, artificial silk, paper, and photographic plates, colloids are involved, and a knowledge of the general behaviour of colloids throws much light on these and other industrial operations. Many dyes give colloidal solutions, and dyeing, in a large number of cases at any rate, depends on the adsorption of the colouring matter by the fibre. The relation between hide and tannin appears to be of the same description, and the investigation of the tanning process from this point of view shows the definite bearing which colloid and adsorption phenomena have on this operation. The problem of sewage disposal also is closely related to colloid chemistry, and it has been found practicable to retain the colloids of the sewage in the form of adsorption compounds. The tints of coloured glasses are frequently due to the presence of metals in the colloidal state. This is notably the case with gold ruby glass, which owes its colour to the presence of ultramicroscopic particles of the metal. Colloid chemistry has an important bearing, too, on

agricultural chemistry. Many of the properties of soils—for example, permeability, absorptive power, and moisture content—depend more on the size of the constituent particles than on their chemical composition. The retention by the soil particles of materials of nutritive value for plants is closely related to the phenomenon of adsorption already discussed, and it has, in fact, been shown that the removal of dissolved substances by soil from solutions of different concentrations takes place in harmony with the adsorption formula. Colloids are of importance further in connection with the pottery trade. Highly plastic clays behave like colloids, and the treatment of clay with a colloid, such as tannin, notably increases the plasticity of the material. On the view that the plasticity of a clay is determined mainly by its colloid content, and that the latter is chiefly responsible for the power of the clay to adsorb colouring matters, attempts have been made to utilise the adsorptive power of clays, say, for malachite green, as a measure of relative plasticity.

Colloid clay has been found to be capable of use as a catalyst in processes of oxidation and hydrogenation.

Of great interest are recent attempts to interpret the properties of many alloys in terms of colloid chemistry. The view is taken that the technical and physico-chemical properties of an alloy are largely dependent on the state of division of the constituent particles, and that in many cases the size of these particles is such as to bring them within the colloid range. The relation between tempering carbon and hardening carbon, is on these lines described as a 'dispersion allotropy' (For development of this point of view, see Benedicks, Journ Iron and Steel Inst 1905, 352; Koll. Zeitschrift, 1910, 7, 290.)

Reference has been made above to the protective action of emulsion colloids, and this phenomenon is of frequent occurrence. The presence of such colloids, generally and vaguely referred to as 'organic matter,' may altogether prevent the flocculation and precipitation of insoluble compounds. In presence of gelatin, for example, silver nitrate gives with sodium chloride only an opalescence which is not altered by filtration. This is a fact of the greatest importance in connection with photographic emulsions. Closely related to this phenomenon is the use of glues and gums as retarders in the setting of plaster of Paris, and the inclusion of such materials in mixtures which have for their object the prevention of scale in boilers. Detailed references to the bearing of colloid chemistry on technical problems will be found in a monograph, Die Bedeutung der Kolloide für die Technik (Dresden, 1909), by K. Arndt; in a paper on Colloid Chemistry and some of its Technical Aspects, by J. Alexander (J. Soc. Chem. Ind. 1909, 28, 280); in W. W. Taylor's book on The Chemistry of Colloids, 1915; and in Wo. Ostwald's volume, Theoretical and Applied Chemistry, 1917.   J. C. P.

COLLOPHANITE. A colloidal hydrated phosphate and carbonate of calcium forming an important constituent of phosphorites and rockphosphates. It is amorphous and optically isotropic, and forms concretionary masses resembling opal or gum in appearance, with a

vitreous to resinous lustre and a conchoidal fracture. The material may be opaque or translucent to nearly transparent, and the colour ranges through colourless, white, yellow, brown, and reddish. An earthy variety is known as *monite*. Sp.gr. 2·69-2·77 (of monite 2·1); hardness 4½; refractive index 1·568-1·612. A. Lacroix (1910) gives the formula as :—

$$x[Ca_3(PO_4)_2]+yCaCO_3+zH_2O$$
$$x[(CaF)_2Ca_3(PO_4)_6]+yCaCO_3+zH_2O$$
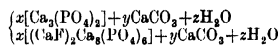
which includes also the variety called *fluocollophanite*. W. T. Schaller (1911) gives the formula as $9CaO \cdot 3P_2O_5 \cdot CaO \cdot CO_2 \cdot H_2O + nH_2O$. The mineral is found in three classes of deposits : in guano deposits, having been first recognised in the guano of Sombrero, West Indies ; in pockets of phosphorites ; and in the phosphatic nodules and coprolites of sedimentary rocks ranging in age from the Eocene to the Silurian. Material of the last of these modes of occurrence frequently contains fluorine in addition to carbonate and phosphate, and is distinguished as *fluocollophanite*.   L. J. S.

COLLOTYPE *v.* PHOTOGRAPHY.

COLOCYNTH. *Bitter apple. Colocynthidis Pulpa*, B P. ; *Colocynthis*, U.S.P. (*Coloquinte*, Fr. ; *Koloquinte*, Ger.)

The dried pulp of the fruit, freed from seeds, of *Citrullus Colocynthis* (Schrader), a climbing plant of the gourd family, inhabiting the warm dry districts of the Old World—India, Persia, Arabia, Syria, and the African and European shores of the Mediterranean. It is cultivated in Spain and Cyprus (*Cf.* Bentl. a. Trim. **114.**)

The B P and U.S.P. demand that not more than 2 p c. of fixed oil be extracted by petroleum spirit (*v.* Dowzard, Pharm. J. 1903, 71, 400). The B.P. demands at least 9 p.c. of ash, the U S P not more than 15 p.c.

Chattaway and Moor (Analyst, 1903, 28, 205) consider 8 p.c. a more reasonable minimum ; Umney (Pharm. J. 1903, 71, 879) found the ash to vary from 7 2-13 5 p.c., and thinks a microscopical examination and the estimation of fixed oil better ways of detecting impurities. The seeds contain the oil, and only 2·3 p.c. of ash ; as they constitute 75 p.c. of the peeled fruit they raise, when mixed with pulp, the amount of fixed oil, and lower the ash content. The two chief varieties imported are Turkey and Spanish colocynth, of which the former is the whiter, the richer in pulp, and the more esteemed.

Colocynth was well known to Greek, Roman, and Arabian medicine, and in the form of solid extract enters into many of the purgative pills of modern pharmacy.

Power and Moore, who gave an account of the earlier literature (Chem. Soc. Trans. 1910, 97, 99), have cast doubt on the existence of the *colocynhin* and *colocynthitin* of previous investigators. The former substance was described as an extremely bitter glucoside and drastic purgative, soluble in water and alcohol, but not in ether, the latter substance as insoluble in water, but soluble in ether. Power and Moore examined the pulp of the fruit separately from the seeds, and the following substances were isolated : *citrullol*, a dihydric alcohol $C_{22}H_{44}O_2(OH)_2$, m.p. 285°-290°, yielding a

diacetyl derivative, melting at 167°; an amorphous alkaloidal substance possessing an extremely bitter taste and representing one of the purgative principles of the fruit; a-elaterin (*see* ELATERIUM); a small amount of hentriacontane $C_{31}H_{64}$, m.p. 68°; a phytosterol $C_{27}H_{46}O$; and a mixture of fatty acids. The seeds, which represent 75·5 p.c. of the peeled fruit, were found to contain traces of an alkaloidal principle, a small amount of an enzyme hydrolysing β-glucosides, and fatty oil. The proportion of glucosidal substance in the fruit is found to be very small. The purgative action depends on at least two compounds, one of which is alkaloidal. After removal of the alkaloidal compound, the fruit still possesses marked purgative properties, but the substance to which these are due has not yet been obtained in a definite form.

It has been sometimes required to search for colocynth in beer (*v.* Dragendorff, Chem. Zentr. 1881, 285, 299). G. B.

COLOGNE YELLOW *v.* CHROMIUM.
COLOPHON *v.* OLEO-RESINS.
COLOPHONY *v.* RESINS.
COLOPTENE *v.* RESINS.
COLORIMETERS, CHROMOMETERS, or **CHROMATOMETERS.** Under this heading are included those instruments (*colorimeters*) which are used for determining the relative intensity of colour in solutions, and those (*chromatometers, tintometers*) which are used to obtain a numerical record of the hue and intensity of a colour.

Colorimetric measurements depend on obtaining equal intensity of colour in two columns of liquid, one of which contains a known amount of the substance to be estimated. This can be done either (*a*) by varying the *concentration* of one liquid, keeping the lengths of columns equal, or (*l*) by altering the length of one column, keeping the concentration the same.

The first method is used in Nessler's test, in Eggertz' method of estimating carbon in steel, and in the simple colorimeter of the U.S. Geological Survey (Bulletin 422). It is applicable to all colorimetric measurements. The second principle is adopted in most cases because it allows the repeated use of the standard solution and facilitates rapid work. In certain cases, however, *e.g.* in comparing manganese solutions, this method fails, as varying the length of column changes the *hue* as well as the *intensity* of the colour.

·The standard used may be of the same composition as the liquid under examination, or may be made of any suitable materials, but its colour must be identical in *quality* with that of the liquid tested, and its value per unit volume in terms of the substance estimated must be accurately known. Thus the permanent standards used in the estimation of combined carbon in steel are generally made of mixed solutions of *metallic salts*, and in the estimation of ammonia in water a solution coloured with *caramel* and a little *aniline red* has been used (Leeds, Chem. News, 37, 229).

Equality of tint having been obtained, the lengths of the columns are noted, and the comparison is repeated, using, preferably, a different length of column of the standard.

The relative strength of the solutions varies *inversely* as the lengths of the columns, so that

if 1 c.c. of the standard solution correspond with x parts by weight of the substance estimated, the weight of that substance in 1 c.c. of the test solution will be

$$\frac{\text{length of column of standard solution} \times x}{\text{length of column of test solution}}$$

If the strength of the standard differs by more than 10 p.c. from that of the test liquid, it is advisable to dilute one or other before comparison.

For the examination of precipitates, a solution of considerable suspensory power is prepared by dissolving 100 grams of gelatine, 100 grams glacial acetic acid, and 1 gram of salicylic acid (to prevent decomposition of the gelatine by keeping) in 1 litre of distilled water.

The solution is clarified with white of egg and filtered hot. For estimation of sulphuric acid, this solution is charged with barium chloride, and is added to a weak standard solution of sulphuric acid or a sulphate and to the solution to be tested, the two turbid liquids being then compared as above. By the use of other reagents, lime, zinc, and a large number of other substances may be estimated.

A useful colorimeter for general purposes, devised by Mills, is shown in Fig. 1. It consists of a glass jar closed above by a cap of which the length is sufficient to cover the top of the liquid. The cap is perforated in the middle and carries a short tube in which slides a glass rod bent as shown, and supporting, exactly at right angles to the axis of the jar, a flat circular opaque white disc. In the bottom of the jar are laid, one above another, a red and a green glass disc which form a black background to the white disc. When examining solutions of certain colours, a background of a colour other than black may be advantageous, and the white disc itself may be covered by a coloured plate. The white disc is lowered to the bottom of the jar by moving its rod, and the jar is filled to exactly 100 divisions with a standard liquid.

The white disc is raised until, on looking vertically down through the liquid at the disc, the depth of tint appears suitable. A second apparatus is then filled to 100 divisions with the liquid to be tested and its disc is adjusted until the colours of the columns of liquid in the two jars appear of equal intensity.

By placing on the white disc a small, black, hemispherical button, this instrument may be used for determining the strength of turbid solutions, such as milk, or for ascertaining the amount of a precipitate suspended in a liquid. Milk is diluted before examination with 99 parts of water, and is compared with a similarly diluted milk of known quality, the disc with the button
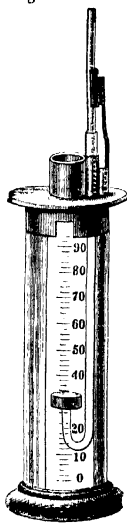

FIG. 1.

being adjusted in each tube as above until just invisible.

The slight alteration in the level of the liquid caused by the varying length of the sliding tube contained in the liquid when adjusting the height of the white disc is found by experiment, and a correction must be introduced into the calculation for variations of more than two or three divisions.

A very useful colorimeter, especially designed for the estimation of carbon in steel, but of course available for other purposes, has been introduced by Stead (Proc. Iron and Steel Inst. 1883, No. 1, 213). A similar, but more convenient apparatus, devised by Ridsdale (J Soc. Chem Ind 1886, 586) is shown in Fig. 2 Three glass tubes, each fitted below with a small,
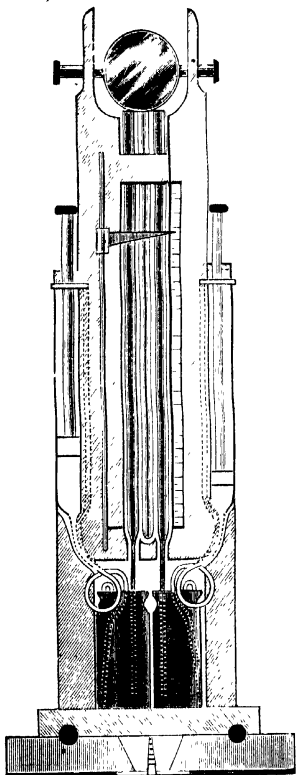

FIG. 2.

opaque, white cylinder, are placed beneath a movable mirror, in a stand which may be turned to any position upon its weighted base. The central tube is removable and is closed below ; the outer tubes are drawn out and pass through indiarubber corks into ruby glass bottles, containing standard solutions of different strengths. Each bottle has a tube with a stopcock through which the liquid may be introduced or removed, and each is connected by a flexible tube with a syringe.

The liquid under examination is introduced into the central tube, and by working the syringes the standard solutions are raised in their tubes until the intensity of colour in each tube, as seen by looking into the mirror which is adjusted to reflect the light passing upwards through the tubes, is identical. Two distinct comparisons are thus simultaneously made, and, by noting the height of each column by means of the sliding pointer, the strength of the tested liquid may be ascertained from the formula already given. A very important advantage of this apparatus is that every part except the central tube is cleansed and recharged without disconnection.

Ridsdale (J. Soc. Chem. Ind. 1888, 70) has devised an apparatus for the examination of liquids of deeper tint than can be used in the foregoing apparatus. The central upper tube (Fig. 3) is sealed below, the upper side tubes are perforated at the bottom. Each tube contains a loose white opaque plug, and each is held at
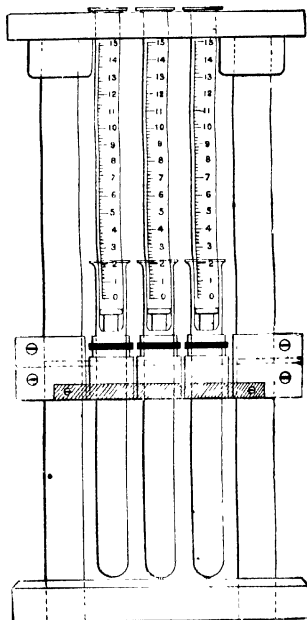

FIG 3

any height by a movable jaw pressed against it by an indiarubber band.

The centre tube is charged with, say, 10 divisions of the standard solution, and the test liquid is run into one of the side tubes, whence it passes at once into the lower tube. When this is nearly filled, it is gradually raised to bring a portion of its contents into the upper

tube, until, on looking down vertically, the colours in the upper side tube and in the standard tube are of equal intensity. The calculation is made as already described. The lower tube beneath the standard tube must be raised with that of the side tube in order to equalise the effect of the double thickness of glass. When the solutions to be tested differ widely in tint, the standard tube may be perforated so that the length of its column may be readily adjusted.

Stokes' apparatus (Chem. Soc Proc 1887, 135) has two tubes placed vertically in a stand with a reflector below One tube is connected with a reservoir of the standard solution, by raising or lowering which the level of liquid in the tube can be altered

A similar arrangement is used in Le Docte's colorimeter (Eng. Pat 20667, 1898).

The Kennicott-Sargent colorimeter (Chem. Engineer, 1907, 213) differs from the above only in altering the level of the standard liquid by moving a glass plunger in a fixed cylindrical reservoir

Another arrangement, in which the standard liquid is forced into a graduated tube from a reservoir, is described by Gunsberg (Dingl poly. J. 228, 457).

The Nesslerising tubes adopted by Hehner (Chem. News, 33, 185) and recommended by Milne (J. Soc. Chem. Ind 1887, 33) are two cylinders of equal and perfectly uniform diameter, holding about 100 c.c Each is graduated from below, and at about the 30 c c. division has a glass stopcock.

The two cylinders are placed side by side on white paper, and to one of them is added 100 c c. of the liquid to be tested, followed by 2 c.c. of Nessler's solution To the other tube a suitable and known amount of standard solution of ammonium chloride is added, and the volume is made up to 100 c.c. with distilled water, after which 2 c.c. of Nessler's solution is added. The two liquids are looked at *vertically*, and the darker is allowed to slowly run off into a clean beaker, until their colours are equal The comparison may be repeated after filling up from the beaker. The mode of calculation is the same as in former cases.

A modified form of Eggertz tube has been described by Hogg (J. Soc. Chem. Ind 1895, 1022).

In a colorimeter devised by Leeds (Chem. News, 37, 229) comparison tubes are arranged in a rack, light being reflected through them by an inclined upper mirror, and again reflected to the eye of the observer from a mirror similarly placed beneath them. The standard liquid is contained in a bottle prism which is moved beneath one of the comparison tubes containing distilled water only until the colour observed is identical with that in the tube containing the test liquid. The strength of the test liquid is calculated from the thickness of liquid in that section of the prism which is interposed.

Gallenkamp's colorimeter (Chem. Zeit. Rep. 1891, 324) consists of two vertical troughs enclosed in a metal frame. That which contains the standard solution is wedge-shaped, while that for the test liquid is rectangular. An observation apparatus, moving vertically over a scale of 100 parts, has two slits at the same level, one

opposite each trough, the light from which is reflected and brought into one eyepiece. The observation consists in finding the thickness of the stratum of standard solution in the prism, which shows the same depth of colour as the test liquid.

White's apparatus differs from the above in having two wedge-shaped tanks, both movable with reference to two fixed slits through which the depth of colour is observed.

A colorimeter, described by Autenrieth and Koenigsberger (Chem Zentr. 1910. i. 2032) and recommended especially for the determination of hæmatine in blood, depends on comparison of the test liquid with a stable solution of similar hue contained in a wedge-shaped reservoir which is movable vertically beside the trough containing the test liquid. The movement of the wedge is measured on a millimetre scale, and the reading translated directly into percentages by reference to a plotted curve The two colours are observed through a Helmholtz ' Doppelplatte,' which obviates a dividing space in the field of view By substituting a suitable wedge, the instrument can also be used for the estimation of titanium, iron, chromium, iodine, ammonia, nitric acid, &c

Schreiner's colorimeter (J Amer Chem. Soc 1905, 1192) consists essentially of two parts : a wide flat - ended tube, 4 in. about 26 cm × 3 cm , graduated in millimetres, and the flat - ended immersion tube A, about 26 cm × 2 cm , which slides inside the wider tube

Two such pairs of tubes are mounted on a stand (Fig. 4), the inner tubes being fixed to the top of the camera while the outer tubes are held in brass clips which keep them in position, but permit their being moved up and down The length of the column of liquid enclosed between the ends of the outer and inner tubes can thus be adjusted at will Light,

Fig. 4.

reflected from a white surface D, passes through the two columns of liquid, and is then reflected at a mirror E to the observer's eyes at F. The axes of the tubes are inclined to one another so as to bring the images close together. Standard glass slides may be inserted at G in place of one of the wide tubes, the immersion tube being left in position.

Patterson has described (J. Soc. Chem. Ind. 1890, 36) a more complex apparatus employing
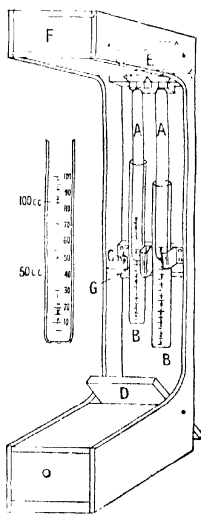
the same principle. In this case the adjustment of the concentric tubes is made by rack and pinion, and total reflection prisms are employed to bring the two images into one eyepiece. By substituting a direct-vision spectroscope for the eyepiece, the apparatus becomes a *spectrum absorptimeter*.

The simple and effective colorimeter devised by Steiger (J. Amer. Chem. Soc. 1908, 215) consists of two wooden boxes painted dead-black inside, one of which (Fig. 5A) is mounted on a
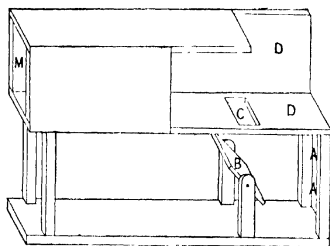

FIG. 5A.

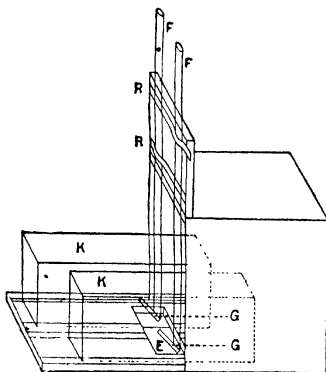stand and has a rectangular opening C in the base, while the second box (Fig. 5B) fits into the

FIG. 5B.

first, and has a rectangular opening, E, which coincides with C.

In the base of this box are two grooves in which slide two rectangular glass cells K, K, about 15 cm. long × 2·5 cm. wide × 5 cm. deep.

Fixed vertically over the opening E are two glass rods F, F, held in place by the springs R, each carrying at the lower end a small plane mirror, G, fixed at an angle of 45°. Light coming through the ground-glass A is reflected by a mirror, B, through the aperture E into the tank, where it is again reflected at the mirror G and passes through a column of liquid, the length of which can be altered by moving the tank backwards and forwards. When equality of colour is obtained, the lengths of the columns are read

off on millimetre scales engraved on the base of each tank. The reading is taken where the lower edge of the mirror touches the bottom of the tank.

Otto's *ozonometer* has two parallel tubes for gases or liquids, and employs wedges of coloured glass moving over a graduated scale as a means of measuring the depth of tint (Eng. Pat. 17524, 1898).

H. Krüss suggests (Zeitsch. anorg. Chem. 5, 325) the application to colorimeters of the Lummer-Brodhun double prism, which gives a field of view in which there is no visible line of separation between the two colours under observation. This condition gives maximum accuracy in matching the colours (*see also* Chem. Soc. Abstr. 1894, ii 158).

Andrieux (Compt. rend. 103, 281) describes an apparatus in which the *quality* and *intensity* of a colour are determined by comparison with a ray of polarised light.

An apparatus has been described by Meisling (Zeitsch. anal. Chem. 1904, 137), in which the hue is matched by the colour of a quartz plate in polarised light, and the intensity is measured by varying the length of the column of liquid.

An ingenious instrument, introduced by Mr. J. W. Lovibond, for the examination of liquids, powders, fabrics, &c., and known as the *tintometer*, is shown, partly in section, in Fig. 6. It
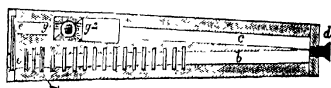

FIG. 6.

consists of a box, closed at one end by a ground glass plate, e, and separated into two divisions b, c. The box is carried by a stand, adjustable to any angle. A square glass cell, of known width, along the line g' g^2, containing the solution to be examined, is placed in one division, and glass plates h of similar colour (or, if necessary, of different colours, producing the proper tint in combination), and of known intensity, are placed in grooves in the other division, until, on looking through both tubes simultaneously through a single eyepiece, d, shaded to prevent access of side light to the eye, the appearance through the glass plates is identical with that through the solution.

The standard plates are specially prepared of various colours, and each is distinguished by a number indicating its *colour*, and another number showing the *intensity* of colour, i.e. the number of plates of that colour of unit intensity required to produce an intensity equal to that of the plate. The unit chosen by the inventor for each colour is an arbitrary one, but its actual value can be ascertained at any time by comparison with a standard solution of similar colour.

In some cases the glass plate e is wanting, and an adjustable plane glass mirror is used to reflect the light to the apparatus (Eng. Pat. 12867, 1886).

When the colour of a fabric is to be estimated, the fabric is stretched on a block placed in the division c, and a white fabric of *similar texture*, previously compared with a plate of pure *plaster*

of Paris, is placed in the division *b*. The standard plates are then inserted as above until the appearances through the eyepiece are identical. *Powders, sugars, &c.*, pressed in a small tray placed in the division *c*, may be similarly examined, a tray containing pure plaster of Paris being placed in the division *b* (J. Soc. Chem. Ind. 1888, 234).

For very delicate observations, the intensity of the light used may be found and noted, before commencing, by closing the division *c* and placing in the divisions *b* as many standard plates of *neutral tint* as serve to obstruct all the light.

The substitution of a movable wedge of coloured glass for the standard plates makes the apparatus available for ordinary colorimetric determinations (J. Soc. Chem Ind 1888, 234). An improved form of Lovibond's apparatus is binocular, and has a movable diaphragm. This makes it applicable to tests of colour vision (*ibid.* 1891, 489) (*see also* Lovibond, *ibid.* 1909, 500).

Procter has described (*ibid.* 1895, 123) a modified form of tintometer in which, by a system of mirrors, the colours to be compared are brought close together in the field of view, thus giving greater accuracy.

Sczepanik (Eng Pat. 22995, 1907) has patented an ingenious apparatus with which a numerical record of any colour can be obtained. Three strata of liquid of the three primary colours are superimposed. The thickness of each stratum can be measured and altered independently of the others, and thus any hue or intensity of colour can be matched.

Gardner and Dufton have introduced the ' Dalite ' lamp, which gives a light of the quality of daylight, and may be used for tintometric work (J. Soc. Chem. Ind. 1904, 598). This lamp is also of use in performing titrations by artificial light.

A useful device, introduced by Dupré (Analyst, 5, 123), may be mentioned under this heading. In the volumetric estimation of silver with potassium chromate as an indicator, especially when the solution is weak, it is somewhat difficult, on account of the original yellow colour of the solution, to observe the first tinge of red produced by the formation of the silver chromate. Dupré interposes, between the eye and the test liquid, a flat glass cell (of which the faces are about half an inch apart) containing a solution of potassium chromate of such strength as will neutralise the colour of the test liquid, which thus appears perfectly colourless, and in which the faintest appearance of red is readily visible. The cell filled with other liquid may be similarly adopted in many other titrations.

König (Proc. Amer. Phil. Soc. [18] 7, 29, 184, 208, 211) has devised a method for estimating metals by the intensity of the colour imparted by them to the borax bead. He dissolves a known weight of the oxide in a known weight of borax, grinds the bead until its faces are flat, coats it with Canada balsam to render its rough faces transparent, and places it in an apparatus where it is viewed by a lens of small power, while, by means of a rack, a glass prism whose colour is complementary to that under examination, is moved before it until such a thickness is interposed that the colour of the bead is extinguished.

A photochemical process for estimating differences in the intensity of a colour has been described by E. J. Mills and Buchanan (J. Soc. Chem. Ind. 1888, 309). It has been applied to the comparison of dyed goods. A number of discs of the tissues are photographed on one negative from which a number of positives on paper sensitised with silver, are copied. These are treated as usual, soaked for a considerable time in sodium thiosulphate to remove the whole of the unaltered silver salt, well washed, and dried. The disc photographs of each tissue are cut from a number of positives and each set is burned separately. The silver in the residue is dissolved and estimated volumetrically. The relative amount of silver found in the different sets of discs directly represents the relative intensity of the colours.

The following colorimetric process for the estimation of minute quantities of sulphur in iron, mineral waters, black ash, slag, &c., is due to Wiborgh (Chem. Zeit. 10, 92 ; Chem. News, 1886, 54, 158).

The divided metal, ore, &c , or the concentrated solution, is introduced into a small flask provided with an indiarubber cork, through which passes a stoppered funnel for introduction of acid, and a narrow-mouthed funnel ground at the top. A disc of white calico, which has been previously saturated with a solution of 5 grams crystallised *cadmium nitrate* (or, preferably, *cadmium acetate*) in 100 c c. of water and dried in a horizontal position on a cloth, is fixed between two indiarubber rings of the same interior diameters as the standard discs hereafter described, and the rings are firmly clamped over the funnel mouth. Dilute sulphuric acid is poured into the flask and heat is applied. In from 30 to 45 minutes the whole of the sulphur which is capable of conversion into sulphuretted hydrogen has passed off in that form and has been *wholly* absorbed by the cadmium salt on the calico. The disc is removed and compared with a set of standard discs, similarly prepared from iron containing a known amount of sulphur. The standard discs should not be exposed too freely to light. Arsenic, carbon, silicon, and copper do not appear to affect the determination. This method is so delicate that a disc will show a tinge of the yellow colour due to the cadmium sulphide when so small a quantity as the 1000th of a milligram of sulphur is present per square centimetre.

COLOUR AND CHEMICAL CONSTITUTION.

The object of this article is to give as concise a description as possible of the various rules which have been established, and the theories which have been proposed, with regard to the relation between colour and chemical constitution, particularly to the colour of dyes, with special reference to those rules which have proved of value in the preparation of dyes and which have served as guides for modifying the colour in a group of dyes.

Historical Outline.—The first synthetic dye (mauve) was produced by Sir W. H. Perkin in 1856. This branch of synthetic chemistry developed with great rapidity, and in the next twenty years the first members of many important groups of dyes had been prepared, *e.g.* fuchsine (1859), rosaniline blue (1860), and alkylated triphenylmethane dyes (1863–1866) ;

Bismarck brown (1864), chrysoidine (1876), and naphthol orange (1876) in the azo- group; Martius yellow (1864) in the nitro- group; Magdala red (1868) in the azine series; alizarin (1869) of the anthraquinone group; fluorescein and eosin (1874), representing the phthaleins, and Lauth's violet (1876), foreshadowing the thiazines. By this time sufficient material had been accumulated to allow the formulation of the well-known *Witt's Rule* (1876), according to which substances attained the potentiality of colour when their molecules contained certain atomic arrangements or groups, which Witt termed *chromophores*. The colour and dyeing properties were made manifest by the introduction of additional groups termed *auxochromes*.

Within the next three years additional triphenylmethane and azo- dyes were produced, deeper colour (red) being attained in the latter group by the use of naphthalene components in place of the benzene derivatives used in the earlier members, as *e.g.* in the Ponceaus (1878); and also by the introduction of an additional chromophore, as in Biebrich scarlet (1878). A consideration of the results now obtained, especially in the triphenylmethane and azo- groups, led to the enunciation of *Nietzki's Rule* (1879), which states that the colour of a dyestuff can be deepened by adding groups so as to increase its molecular weight, and that the deepening of colour produced is more or less proportional to the increase of molecular weight. (It should be noted that the term *depth* is used by colour-chemists in a very definite and limited way. In ordinary language the term depth of colour has at least two meanings. Blue and red are said to be deeper colours than yellow, and also one yellow is said to be deeper than another yellow if it is stronger or more intense, *i.e.* less admixed with white. Colour-chemists restrict the use of the term, and employ it for the first purpose only. Blue is deeper than red or yellow, and red is deeper than yellow. The ordinary colours arranged according to depth are: green, blue, violet, red, orange, yellow, *i.e.* the complements to the ordinary colours of the spectrum taken in order from the red to the violet end. This rule served for many years as a most valuable guide in extending the range of colours in many groups of dyes, especially in the azo- group, in which the deepest colours were now soon obtained (blue-black, 1882, Glaser). It may be said that this rule is still a valuable guide to the colour chemist.

In 1885 Liebermann and v. Kostanecki published the results of their investigations of the colour and dyeing properties of the hydroxy-derivatives of anthraquinone. Although these authors did not commit themselves to any very definite statement, yet their publication drew the attention of colour-chemists to the ease with which colour could be deepened by the multiplication of auxochrome groups in the molecule, provided these groups were suitably arranged. This general principle may be said to have been of equal value with Nietzki's Rule, and for many years the development of dye manufacture was almost entirely controlled by these two rules. Very interesting and ingenious methods were developed by Bohn and Schmidt in 1888 and 1890 for the multiplication of hydroxyl groups in the anthra-

quinone molecule with the result that a complete range of colours was soon available in this group of mordant dyes. The continued application of the same idea led somewhat later to the preparation of anthraquinone dyes containing both amino- and hydroxyl- groups, such as alizarin saphirol (1898), which combines the advantages of deep colour and fastness with brightness and clearness of tone. Liebermann and Kostanecki's Rule led at once to the careful study and production of dihydroxy-, amino-, hydroxy-, and diamino-naphthalene derivatives and their employment in the manufacture of azo- dyes. This general principle led to the production between the years 1887 and 1897 of an enormous number of azo- dyes of all colours.

In 1888 H. E. Armstrong put forward the best-known theory which has ever been formulated as to the cause of colour in organic compounds. This is known as the *Quinonoid Theory*. Its author pointed out that the chemical formulæ of the well-known dyestuffs either contained the *quinonoid* grouping or could be slightly modified or rearranged, in accordance with accepted ideas on tautomerism, so as to contain this grouping. More recent work has shown that the original quinonoid theory cannot stand. Modifications have been put forward by Baeyer (1907) and H. v. Liebig (1908), neither of which, however, is entirely satisfactory.

Of recent years it has come to be generally recognised that visible colour is only a special case of selective absorption. That some substances are coloured whilst others, nearly related, are colourless, must be regarded as more or less accidental, and due to a physiological cause rather than to any essential physical difference between them, viz. to the fact that the human eye can only detect selective absorption within a limited range of the spectrum. The problem of colour has thus resolved itself into two parts: (1) the cause of selective absorption; (2) the cause of the absorption lying within the limits of the visible spectrum.

As to the cause of selective absorption various theories have been put forward in recent years. We may mention Baly and Desch's theory, according to which absorption bands are due to dynamic isomerism (1904–1905), Stewart and Baly's theory of isotropesis as the cause of selective absorption (1906), Watson and Meek's theory that absorption in the visible spectrum and its neighbourhood is due to the reversal during tautomeric change of a conjugate chain of alternate double and single bonds (1915), the theory that absorption bands in the visible part of the spectrum are due to the vibration of electrons, and Baly's theory (1914) that absorption bands in the visible and ultra-violet parts of the spectrum are due to overtones or summation or difference tones derived from fundamental vibrations causing infra-red absorption bands (infra-red absorption bands have been attributed by most investigators to the vibrations of definite chemical radicals, Abney and Festing (1881), Julius (1888), Coblentz (1904–1905), and Weniger (1910)). In 1897 Pauer showed that under certain circumstances ordinary broad absorption bands are replaced by a large number of fine bands, recalling the lines in the emission spectra of substances examined in flames or under the

influence of the electric discharge. Hartley (1908) came to the conclusion that the ordinary broad absorption bands are formed by the fusion of these narrow bands. Various observers have shown the intimate connection between such fine absorption bands and the lines in the emission spectra of the same substances, *e.g.* Wullner (1863), Mitscherlich (1864), Salet (1872), Eder and Valenta (1899). And, finally, in certain cases (hydrogen and helium) the lines in the emission spectra have been deduced with great accuracy on the hypothesis that they are due to rotational vibration of electrons within the atoms.

The fact that so many different theories have been formulated makes it obvious that no final conclusion has been reached as to the cause of absorption bands in general.

As to the causes which bring the absorption bands into the visible spectrum and influence their positions within the visible spectrum, many investigators showed that Nietzki's rule was only a first approximation to the facts, and many exceptions to this rule were collected by Schütze (1892). Hewitt (1907) suggested that the chief oscillation frequency was less, and consequently the colour was deeper, the longer the conjugate chain of alternate double and single bonds in the molecule. The present writer pointed out in 1914 that those dyes of which the molecular formula can only be written in a quinonoid form have all a deep colour, whilst if the formula can be written either in a quinonoid or a non-quinonoid form, even great molecular complexity may fail to produce any great depth of colour. Watson and Meek (1915) showed that in several series the period of the absorption band is proportional to the length of the conjugate chain, which may be assumed to reverse during tautomeric change.
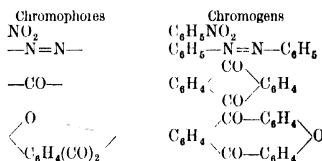
No explanation has yet been offered of the great effect on depth of colour which is so frequently produced by a multiplication of auxochromes. The relative position of the auxochromes has a great effect on the colour. Certain regularities in this respect have been pointed out by Kauffmann and Franck (1906), and Meek and Watson (1916).

It cannot be said that the theories which have been formulated since 1885 have proved of much service for the preparation of dyes. In the older group of dyes a complete range of colours had already been attained by assiduous experiment, guided by Nietzki's and Liebermann and Kostanecki's rules. It may perhaps be claimed that the quinonoid theory had some influence in the development of the azo-pyrazolone dyes. The present writer was able to apply one of the rules which he formulated to the production of deep-coloured dyes from the yellow flavones, and the work in this direction was perhaps of service for the recognition of the molecular structure of the colouring matters of flowers (anthocyanins). As to the new groups of valuable synthetic dyes which have been developed recently, the sulphide dyes, and the anthraquinone vat-dyes, the constitution of the former has been too little understood to allow of anything but empirical investigation, whilst in the latter group (the 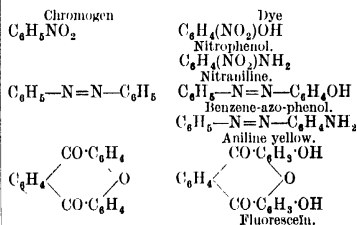anthraquinone vat-dyes), our theories seem at present quite unable to explain the wealth of colour phenomena exhibited by the dyes already synthesised.

A short account is appended of some of the more important theories and rules above mentioned.

Witt's Rule.—This investigator pointed out (Ber. 1876, **9**, 522) that two things are required to give an organic substance colour and dyeing properties. The molecule must possess a certain grouping of atoms to give it the potentiality for colour, and it must also possess a salt-forming radical to bring out the colour and dyeing properties. The atomic groupings giving the potentiality of colour he termed *chromophores*, and molecules containing them were called *chromogens*. He specified the following chromophores and gave illustrations of chromogens containing them :—

Chromophores	Chromogens
NO_2	$C_6H_5NO_2$
$—N=N—$	$C_6H_5—N=N—C_6H_5$
$—CO—$	$C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_6H_4$
$\langle\begin{smallmatrix}O\\C_6H_4(CO)_2\end{smallmatrix}$	$C_6H_4\langle\begin{smallmatrix}CO—C_6H_4\\CO—C_6H_4\end{smallmatrix}\rangle O$

It will be noticed that some of the chromogens are colourless, *e.g.* nitrobenzene and phenolphthalein, whilst others have a feeble colour, *e.g.* azobenzene and anthraquinone ; but none of the chromogens has any dyeing property. The colour is developed or strengthened by the introduction of salt-forming radicals into the chromogens. These radicals he therefore termed *auxochromes.* Hydroxyl, amino- and substituted amino- groups, *e.g.* $NHCH_3$, $N(CH_3)_2$, &c., are the principal auxochromes. Not all salt-forming groups can act as auxochromes, *e.g.* sulphonic and carboxyl groups are without this function. The following table shows how the chromogens already mentioned are converted into dyes by the introduction of auxochromes :—

Chromogen	Dye
$C_6H_5NO_2$	$C_6H_4(NO_2)OH$ Nitrophenol.
	$C_6H_4(NO_2)NH_2$ Nitraniline.
$C_6H_5—N=N—C_6H_5$	$C_6H_5—N=N—C_6H_4OH$ Benzene-azo-phenol.
	$C_6H_5—N=N—C_6H_4NH_2$ Aniline yellow.
$C_6H_4\langle\begin{smallmatrix}CO·C_6H_4\\CO·C_6H_4\end{smallmatrix}\rangle O$	$C_6H_4\langle\begin{smallmatrix}CO·C_6H_3·OH\\CO·C_6H_3·OH\end{smallmatrix}\rangle O$ Fluorescein.

## THE QUINONOID AND MODIFIED QUINONOID THEORIES.

In 1888 (Proc. Chem. Soc. 1888, 27–33). H. E. Armstrong pointed out that the chemical formulæ of the well-known dyestuffs either contained the *quinonoid* grouping or could be slightly modified or rearranged, in accordance with accepted ideas on tautomerism, so as to contain this grouping. The *quinonoid* grouping may be defined as a benzene nucleus to which

other atoms or groups are attached by double bonds in the *para-* or *ortho-* positions :

$$= \bigcirc = \quad \text{or} \quad =\bigcirc$$
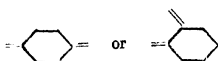
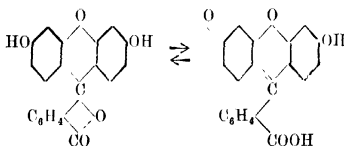Armstrong was probably much impressed by the recently discovered fact that benzene-azo-β-naphthol was identical with the phenyl hydrazone of β-naphthoquinone, so that there was as much justification for the formula
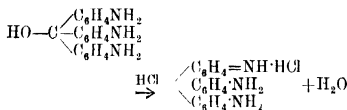
$$C_6H_5NH—N=\bigcirc\!\!\!\bigcirc \!\! O$$
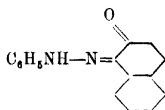
as for the more usual one based on the formation of the substance from β-naphthol and a benzene-diazonium salt, viz. :

$$C_6H_5N=N—\bigcirc\!\!\!\bigcirc^{HO}$$
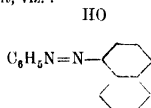
and if it were allowable to assume tautomerism to a quinonoid form in this case, it might be allowable in other cases, *e.g.* in the case of fluorescein :

$$HO\bigcirc\!\!\!\bigcirc\!\!\!\bigcirc OH \rightleftharpoons \bigcirc\!\!\!\bigcirc\!\!\!\bigcirc OH$$
$$\underset{\substack{| \\ C_6H_4\\ |\\ CO}}{C} \qquad \underset{\substack{|\\ C_6H_4\\ |\\ COOH}}{C}$$

whilst in the case of *p*-rosaniline it was quite consistent with experimental fact to suppose that on the conversion of the base into salts there was elimination of a molecule of water and formation of a substance with a quinonoid structure :

$$HO—C\!\!\!\underset{\diagdown C_6H_4NH_2}{\overset{\diagup C_6H_4NH_2}{—C_6H_4NH_2}}$$
$$\overset{HCl}{\Rightarrow} \quad \underset{\diagdown C_6H_4\cdot NH_2}{\overset{\diagup C_6H_4=NH\cdot HCl}{C_6H_4\cdot NH_2}} \quad +H_2O$$
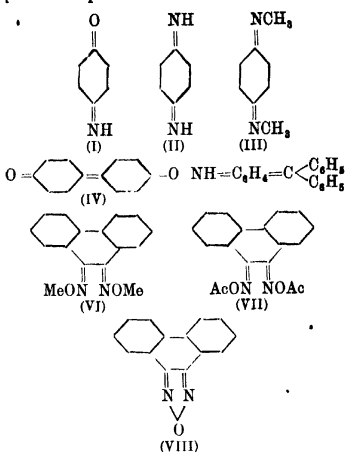
In many cases the ordinary formula already contained the quinonoid structure.

The theory has been shown to be untenable. On the one hand, substances have been prepared which have a quinonoid structure, but are colourless, and on the other hand, coloured substances are known to which a quinonoid structure cannot be assigned.

Colourless Substances possessing a Quinonoid Structure.—Iminoquinone (I), diiminoquinone (II), quinonedimethylimine (colourless in crystalline form, yellow in solution) (III), diphenoquinone (exists in two modifications, one of which is colourless) (IV), and fuchsonimine (V); also the dimethyl ether (VI), the diacyl

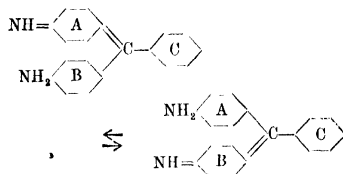derivatives (VII), and the anhydride (VIII) of phenanthraquinone dioxime :—

$$\underset{(I)}{\overset{O}{\underset{NH}{\bigcirc}}} \quad \underset{(II)}{\overset{NH}{\underset{NH}{\bigcirc}}} \quad \underset{(III)}{\overset{NCH_3}{\underset{NCH_3}{\bigcirc}}}$$

$$O=\bigcirc=\!\!\!-O \quad NH=C_6H_4=C\!\!<\!\!\overset{C_6H_5}{\underset{C_6H_5}{}}$$
$$(IV) \qquad\qquad (V)$$

$$\underset{(VI)}{\overset{MeON\;NOMe}{\bigcirc\!\!\!\bigcirc}} \qquad \underset{(VII)}{\overset{AcON\;NOAc}{\bigcirc\!\!\!\bigcirc}}$$

$$\underset{(VIII)}{\overset{\bigcirc\!\!\!\bigcirc}{\underset{\underset{O}{\overset{\|}{N\;\;N}}}{}}}$$

Coloured Substances to which a Quinonoid Structure cannot be assigned.—Nitroquinol dimethyl ether, the sulphate of *p*-trichlortriphenyl carbinol, the fulvenes, *e.g.* dimethylfulvene, and some fatty compounds, such as diacetyl, tertiary nitroso- compounds, *e.g. tert*-nitrosobutane, and dinitroparaffins.

Baeyer's Modification of the Quinonoid Theory.—It has already been mentioned that fuchsonimine is colourless. The introduction of a *para-* amino group into one of the phenyl groups causes the development of colour :

$$\underset{C_6H_5}{\overset{p\text{-}NH_2\cdot C_6H_4}{>}}C=\bigcirc=NH$$
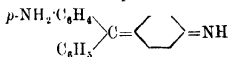
This and similar facts led A. v. Baeyer to suggest that the cause of colour is an oscillation of the quinonoid condition between two or more benzene nuclei (Jour. Chem. Soc. Abs. 1907, i. 504). If we call the three benzene nuclei in the above compound A, B, and C, it will be seen that the oscillation of a hydrogen atom will allow A and B alternately to become quinonoid :

$$\underset{NH_2\diagdown B}{\overset{NH=\diagup A}{\bigcirc}}\!\!>\!\!C—\langle\;C\;\rangle$$

$$\underset{NH=\diagdown B}{\overset{NH_2\diagup A}{\bigcirc}}\!\!>\!\!C—\langle\;C\;\rangle$$

Baeyer suggested that this oscillation was the cause of the colour.

Many strongly-coloured substances are known in which such an oscillation is not possible. And necessarily all the arguments against the original quinonoid theory apply with still greater force against this modified quinonoid theory.

$$\overset{\|}{A}\quad\overset{\|}{A}\quad\overset{\|}{A}$$

H. v. Liebig's Theory that —A—A—A— is the Essential Organic Chromophore.—The fact that the fulvenes are coloured, although they do not contain the quinonoid structure, led H. v. Liebig to suggest that the essential cause of colour is the arrangement of linkages which is possessed both by quinonoid compounds and the fulvenes, viz. —A—A—A— (Annalen, 1908, 360, 128)   This theory explains the colour of nitroquinol dimethyl ether, which contains this arrangement of linkages :—

OMe
|
C
C   C—N
C
C
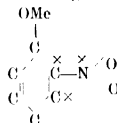
The theory will not explain the colour of the tertiary fatty nitroso- compounds; and, of course, the existence of colourless quinonoid compounds is as much an argument against this modification as against the original quinonoid theory

NIETZKI'S RULE   The colour of a dyestuff can be deepened by adding groups so as to increase its molecular weight, and the deepening of colour produced is, more or less, proportional to the increase of its molecular weight (Verhandl des Vereins zum Beförderung des Gewerbefleisses, 1879, 58, 231). This rule was probably formulated by Nietzki to summarise well-known facts in connection with the triphenylmethane group of dyes, but apparently was not based on any systematic investigation. The table on p. 349 shows that the rule applies to a considerable extent to other groups besides the triphenylmethane series.

The rule was subjected to a careful examination by Schutze (Zeitsch physikal. Chem. 1892, 9, 109 et seq.), who pointed out many exceptions. He showed that in some cases, e g. on the addition of a nitro- group to indigo, the shade even becomes lighter instead of deeper, and he introduced the terms bathychrome and hypsochrome, the former being applied to those groups which produce a deepening of colour, and the latter to those having the contrary effect. Another example of a hypsochrome is the acetyl group. All dyestuffs containing hydroxyl- or amino-groups become much lighter in colour when completely acetylated.

The following table is of interest, as showing that in some cases the molecular weight may be made very large without a deep colour being attained.

| Molecular formula	Mol wt.	Shade of dyeing
C_6H_5—N=N—C_6H_4OH	198	yellow
C_6H_5—N=N—C_6H_4—N=N $C_6H_3{}^{OH}_{COOH}$	346	brownish yellow
C_6H_5—N=N- C_6H_4—N=N—C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$	450	brownish yellow
C_6H_5—N=N—$C_8H_4{}^{OH}_{C_6H_5}$	274	orange
C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$ | C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$	482	yellow
(OH)(C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$ C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$ C_6H_4—N=N—$C_6H_3{}^{OH}_{COOH}$	752	yellow

HEWITT'S RULE   This investigator's researches on the colour of azo- compounds led him to the conclusion that the chief oscillation frequency is less, and consequently the colour is deeper, the longer the conjugate chain, i.e. the chain of alternate double and single bonds, in the molecule (Chem. Soc Trans. 1907, 91, 1251).

He noticed that in the case of many azo-dyes the introduction of a nitro- group into the benzene nucleus not containing auxochromes produced very pronounced deepening of colour in alkaline solution, e.g p-nitrobenzeneazophenol and p-nitrobenzeneazonaphthol have much deeper colours (crimson and violet) than benzeneazophenol and benzeneazonaphthol (orange and crimson respectively). He brought forward evidence in favour of the assumption that in alkaline solution these nitro- derivatives have an iso- nitroso structure, and in this form the nitro- derivatives have a much longer conjugate chain than the parent substances, e.g. :—
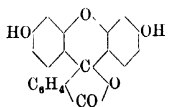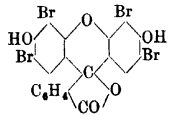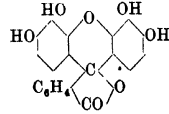
KO
      N=   =N—N=   =O
O

compared with :

      —NH—N=   =O
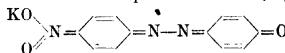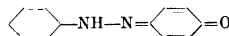
Sircar (Chem. Soc. Trans 1916, 109, 757, et seq.) showed that in very similar azo- compounds the length of the conjugate chain is not proportional to the depth of colour, e.g. 4-nitronaphthalene-1-azophenol only gives a red colour in alkaline solution, whilst p-nitrobenzene-azo-α-naphthol dissolves in the same solvent with a blue colour, whilst the two substances

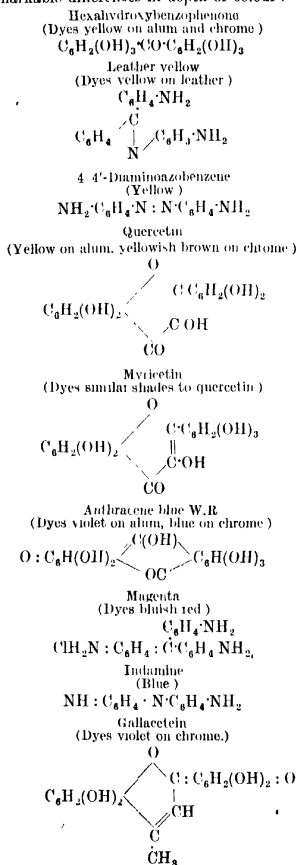| Name	Molecular formula	Mol. wt.	Shade of dyeing
Pararosaniline .	$C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4=NH_2Cl \end{cases}$	281·5	Magenta
Methyl Violet R	$C\begin{cases} C_6H_4NHCH_3 \\ C_6H_4NHCH_3 \\ C_6H_4=NHCH_3Cl \end{cases}$	323·5	Reddish violet
Methyl Violet 3B	$C\begin{cases} C_6H_4\cdot N(CH_3)_2 \\ C_6H_4\cdot N(CH_3)_2 \\ C_6H_4=N(CH_3)_2Cl \end{cases}$	365·5	Violet
Rosaniline Blue	$C\begin{cases} C_6H_4NHC_6H_5 \\ C_6H_4\cdot NHC_6H_5 \\ C_6H_4=NHC_6H_5\cdot Cl \end{cases}$	509·5	Blue
Iodine Green .	$C\begin{cases} C_6H_4\cdot N(CH_3)_2 \\ C_6H_4N(CH_3)_2+CH_3I \\ C_6H_4=N(CH_3)_2I \end{cases}$	599	Green
Benzene-azo-phenol .	$C_6H_5-N=N-C_6H_4OH$	198	Yellow
Benzene-azo-naphthol.	$C_6H_5-N=N-C_{10}H_6OH(\beta)$	248	Red
Biebrich Scarlet . .	$SO_3H\cdot C_6H_4-N=N-C_6H_3(SO_3H)$ $-N=N-C_{10}H_6\cdot OH(\beta)$	512	Red
Naphthol Black . .	$(SO_3H)_2C_{10}H_5-N=N-C_{10}H_6-$ $N=N-C_{10}H_4\begin{cases}OH \\ (SO_3H)_2\end{cases}$	772	Black
Alizarin	$C_6H_4\begin{cases}CO \\ CO\end{cases}C_6H_2(OH)_2$	240	Red (on alum)
Alizarin Bordeaux	$(OH)_2C_6H_2\begin{cases}CO \\ CO\end{cases}C_6H_2(OH)_2$	272	Bordeaux (on alum)
Alizarin Cyanine	$(OH)_2C_6H_2\begin{cases}CO \\ CO\end{cases}C_6H(OH)_3$	288	Violet (on alum)
Fluorescein		332	Yellow
Eosin		648	Red
Gallein .		364	Violet to blue (according to mordant.)
Indigotin . .	$C_{16}H_{10}N_2O_2$	262	Indigo blue
Ciba Blue BB (Tetrabromindigotin)	$C_{16}H_6N_2O_2Br_4$	578	Greenish blue

have conjugate chains of the same length. He came to the conclusion that in azo- dyes the depth of colour is proportional to the length of the conjugate chain reckoned from the auxochrome to the azo- linkage.

WATSON'S RULE.—The present writer pointed out (Proc. Chem. Soc. 1913, 29, 348 ; Chem. Soc. Trans. 1914, 105, 759) that dyes which are quinonoid in all possible tautomeric forms have a deep colour, no matter how simple their structure or how small their molecular weight.

'In the following table there are placed opposite each other in the two columns dyes of very similar constitution which yet show remarkable differences in depth of colour :—

Hexahydroxybenzophenone
(Dyes yellow on alum and chrome)

$$C_6H_2(OH)_3 \cdot CO \cdot C_6H_2(OH)_3$$

Leather yellow
(Dyes yellow on leather)

$$C_6H_4 \cdot NH_2$$

$$C_6H_4 \begin{array}{c} C \\ | \\ N \end{array} C_6H_3 \cdot NH_2$$

4 4'-Diaminoazobenzene
(Yellow)

$$NH_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NH_2$$

Quercetin
(Yellow on alum. yellowish brown on chrome)

$$C_6H_2(OH)_2 \underset{CO}{\overset{C \cdot C_6H_2(OH)_2}{\diagup\diagdown}} C \cdot OH$$

Myricetin
(Dyes similar shades to quercetin)

$$C_6H_2(OH)_2 \underset{CO}{\overset{C \cdot C_6H_2(OH)_3}{\diagup\diagdown}} C \cdot OH$$

Anthracene blue W.R
(Dyes violet on alum, blue on chrome)

$$O : C_6H(OH)_2 \underset{OC}{\overset{C(OH)}{\diagup\diagdown}} C_6H(OH)_3$$

Magenta
(Dyes bluish red)

$$C_6H_4 \cdot NH_2$$

$$ClH_2N : C_6H_4 : C \cdot C_6H_4 \cdot NH_{2,}$$

Indamine
(Blue)

$$NH : C_6H_4 \cdot N \cdot C_6H_4 \cdot NH_2$$

Gallacetein
(Dyes violet on chrome.)

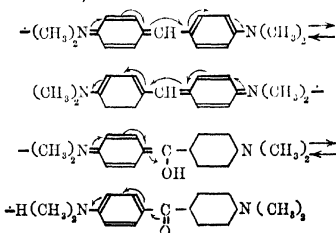$$C_6H_2(OH)_2 \underset{\underset{CH_3}{C}}{\overset{C : C_6H_2(OH)_2 : O}{\diagup\diagdown}} CH$$

'The dyes in the right-hand column can only be represented by formulæ containing a quinonoid arrangement. Whatever tautomeric change they may be supposed to undergo their formulæ still contain the quinonoid arrange-

ment. Those on the left hand differ in that they can be represented by formulæ not containing this arrangement. They can, of course, be supposed to tautomerise into forms containing this quinonoid arrangement, but in all cases it is possible to represent them also in a non-quinonoid form.' 'A survey of all the better known dye-stuffs fully bears out this theory. The triphenylmethane dyes, the pyronines, benzeins, and fluorones, the indophenols, indamines, oxazines, thiazines, azines (safranines, &c.), all satisfy this requirement and exhibit deep colour, in many cases with little molecular complexity. Hæmatein and brazilein conform to this rule. They have almost the same molecular weight as the flavones, and there is considerable resemblance in their structure , but they conform to this rule, whilst the flavones do not, and consequently their colour is much deeper. The alizarin series, and also naphthazarin, illustrate the rule. On the other hand, the monoketonic dyes, e.g. the benzophenone and xanthone derivatives, the flavones and flavonols, ellagic acid, and the azo- dyes can be represented by non-quinonoid formulæ ; and many members of these groups, despite very considerable molecular complexity, have no great depth of colour.'

WATSON'S AND MEEK'S MODIFICATION OF HEWITT'S RULE.— In passing from one tautomeric form to another there is a reversal of the conjugate chain, so that double and single bands change places all along the conjugate chain In that group of substances which can only tautomerise from one quinonoid form to another the conjugate chain reversed is generally longer than in the other group of substances which can tautomerise from a quinonoid to a non-quinonoid form. An appreciation of this fact led to the formulation of a further modification of Hewitt's rule, viz. that the colour is deeper the longer the conjugate chain reversed during tautomeric change (Watson and Meek, Chem. Soc. Trans. 1915, 107, 1567). This rule was tested by measuring the wave-lengths of the maxima of the absorption bands of seven pairs of substances which were selected as being very similar in structure, but having conjugate chains of different lengths reversed during tautomerism. It was found that in each of these seven pairs the period of the vibration was proportional to the length of the conjugate chain reversed (see table, p. 352).

The reversal of the chain is shown in the following structural formulæ for 4 : 4'-tetramethyldiaminobenzhydrol (Michler's hydrol) and 4 : 4'-tetramethyldiaminobenzophenone (Michler's ketone) :—

$$-(CH_3)_2N \diagdown\diagup CH \diagdown\diagup N(CH_3)_2 \rightleftharpoons$$

$$(CH_3)_2N \diagdown\diagup CH \diagdown\diagup N(CH_3)_2 -$$

$$-(CH_3)_2N \diagdown\diagup \underset{OH}{C} - \diagdown\diagup N(CH_3)_2 \rightleftharpoons$$

$$-H(CH_3)_2N \diagdown\diagup \underset{\underset{O}{||}}{C} - \diagdown\diagup N(CH_3)_2$$

Name	Molecular formula	Shade of dyeing
Alizarin	$C_6H_4\genfrac{}{}{0pt}{}{CO}{CO}C_6H_2(OH)_2$	Red (on alum)
Alizarin Bordeaux	$(OH)_2C_6H_2\genfrac{}{}{0pt}{}{CO}{CO}C_6H_2(OH)_2$	Bordeaux (on alum)
Alizarin Cyanine	$(OH)_2C_6H_2\genfrac{}{}{0pt}{}{CO}{CO}C_6H(OH)_3$	Violet (on alum)
Fluorescein		Yellow
Gallein		Violet to blue (according to mordant)
Aniline Yellow	$C_6H_4{-}N{=}N{-}C_6H_4NH_2$	Yellow
Chrysoidine	$C_6H_4{-}N{=}N{-}C_6H_3(NH_2)_2$	Orange
Azoorseilline	$C_6H_4{-}N{=}N{-}C_{10}H_5(SO_3H)OH$	Brownish-red
Congo Violet	$C_6H_4{-}N{=}N{-}C_{10}H_5(SO_3H)OH$ ditto (isomeric)	Violet
Congo Red	$C_6H_4{-}N{=}N{-}C_{10}H_5(SO_3H)NH_2$	Red
Naphthocyanine	$C_6H_4{-}N{=}N{-}C_{10}H_5(SO_3H)NH_2$ $C_6H_4{-}N{=}N{-}C_{10}H_4(SO_3H)(OH)_2$	Blue
Diamine Black, B	$C_6H_4{-}N{=}N{-}C_{10}H_4(SO_3H)(OH)_2$ $C_6H_4{-}N{=}N{-}C_{10}H_4(SO_3H)(OH)(NH_2)$ $C_6H_4{-}N{=}N{-}C_{10}H_4(SO_3H)(OH)NH_2$	Black
Diamine Blue, BB	ditto (isomeric)	Blue
Brasilein		Red
Haematein		Blue

	Length of conjugate chain reversed during tautomerism	Wave-length of absorption band
4 : 4'-Tetramethyldiaminobenzhydrol	$\dfrac{5}{3}$ ratio $= 1\cdot6$	$\dfrac{6100}{3680}$ ratio $= 1\cdot65$
4 : 4'-Tetramethyldiaminobenzophenone		
4 : 4'-Diaminobenzhydrol	$\dfrac{5}{3}$ ratio $= 1\cdot6$	$\dfrac{5640}{3414}$ ratio $= 1\cdot65$
4 : 4'-Diaminobenzophenone		
Quercetin reduction product	$\dfrac{5}{3}$ ratio $= 1\cdot6$	$\dfrac{6100}{3690}$ ratio $= 1\cdot65$
Quercetin		
Morin reduction product	$\dfrac{5}{3}$ ratio $= 1\cdot6$	$\dfrac{5860}{3800(?)}$ ratio $= 1\cdot54(?)$
Morin		
Apigenin reduction product	$\dfrac{5}{3}$ ratio $= 1\cdot6$	$\dfrac{5700}{3410}$ ratio $= 1\cdot67$
Apigenin		
Pyronine G	$\dfrac{4}{3}$ ratio $= 1\cdot3$	$\dfrac{5480}{3861}$ ratio $= 1\cdot41$
3·6·Tetramethyldiaminoxanthone		
3·Hydroxyfluorone	$\dfrac{4}{3}$ ratio $= 1\cdot3$	$\dfrac{5049}{3810}$ ratio $= 1\cdot32$
3·6·Dihydroxyanthone		

EFFECT OF MULTIPLICATION OF AUXOCHROMES ON DEPTH OF COLOUR

Additional auxochromes frequently deepen the colour to a very great extent. This may be regarded as an example of Nietzki's rule, but the effect produced is generally much greater than we should expect from the very moderate weight of the additional auxochromes, e.g. from the first table given in the paragraph on Nietzki's rule, it will be observed that two hydroxyl groups added to fluorescein (producing gallein) deepen the colour much more than four bromine atoms (producing eosin), although their weight is much less. The table on page 351 illustrates the great effect of additional auxochromes

The relative positions of the auxochromes has a very great effect on the colour, e.g. there are two isomeric hexahydroxyanthraquinones, anthracene blue WR and rufigallol, one of which is blue and the other brown.

From a study of the polyhydroxyanthraquinones, Meek and Watson (Chem. Soc. Trans. 1916, 109, 557, et seq.) suggested the following rules as to the influence on the colour of the relative positions of the auxochromes :—

(a) Two hydroxyl groups in one benzene nucleus in the o- or p-position with respect to one another are necessary to produce a deep colour.

(b) The colour is still further deepened if both benzene nuclei contain pairs of hydroxyl groups in the o- or p-position to one another.

(c) Three hydroxyl groups in the 1 : 2 : 4-position in one benzene nucleus produce a deeper colour than a pair of hydroxyl groups in the o- or p-position.

(d) Three hydroxyl groups in the 1 : 2 : 3-position in one benzene nucleus produce a brown colour.

And these rules are apparently applicable to all groups of dyes, e.g. :—

(a) The hydroxy- derivatives of azobenzene dissolve in potash with the following colours :—

p-Hydroxyazobenzene	.	Yellow
o-Hydroxyazobenzene	.	Yellow
Benzeneazoresorcinol	.	Orange
Benzeneazocatechol .	.	Carmine
Benzeneazoquinol .	.	Blue
Benzeneazopyrogallol	.	Brick-red

(b) Fluorescein, quinolphthalein, and catecholphthalein dissolve in potash with a yellow colour ; hydroxyquinolphthalein gives a cherry-red, gallein a blue, and phloroglucinolphthalein an orange under the same conditions.

(c) The same rules are seen to apply to the pyranol dyes.					E. R. W.

COLUMBIA BLACK, -BLUE, -GREEN v. AZO- COLOURING MATTERS.

COLUMBIA YELLOW v. PRIMULINE AND ITS DERIVATIVES.

COLUMBIC ACID, COLUMBAMINE, and **COLUMBIN** v. CALUMBA.

COLUMBITE. A columbate (niobate) of iron, usually containing some manganese ('manganocolumbite') and tantalum, the general formula being $(Fe,Mn)(Cb,Ta)_2O_6$. With an increase in the amount of tantalum, there is a transition to the isomorphous species, *tantalite* (q.v.). The orthorhombic crystals are dark brown or black and opaque, and range in sp.gr. from 5·3 (columbite) to 7·3 (tantalite). It was in this mineral that C. Hatchett discovered, in 1802, the element columbium, so named because the specimen he examined came from America. Columbite is usually found as single crystals embedded in pegmatite or granite ; for example, at Haddam and Middletown in Connecticut, Chesterfield in Massachusetts, brilliant crystals in granite at Standish in Maine, large masses up to 2000 lbs. in granite veins in the Black Hills of South Dakota, and at several other American localities. At Ivigtut in Greenland it has been found in the cryolite deposit. Large crystals are found in the felspar quarries near Moss in Norway. Other localities are Rabenstein in Bavaria, Bushman Land in South Africa, Madagascar, &c.					L. J. S.

COLUMBIUM (*Niobium*). Sym. Cb. At. wt. 93·1 (Smith and van Haagen). Although this metal is still commonly termed niobium by the mineralogist and the metallurgist, the name columbium, which was given to it in 1802 by Hatchett, who first isolated it in the form of a new 'earth' (Cb_2O_5) from a mineral found in Connecticut, has been officially adopted by the chemist in English-speaking countries, and generally throughout the world, except perhaps in Germany.

Columbium is a member of a group of comparatively rare metals, including tantalum, tungsten, molybdenum, titanium, and uranium, commonly occurring together in minerals found in the oldest Plutonic rocks and especially in and around intrusions which traverse pegmatites and other extremely coarse-grained granite rocks. Monazite, and other minerals containing metals of the cerium group, zircons, cryolite, and fluorspar, and minerals containing lithium, cæsium, and rubidium, are often associated with these minerals, and are probably intimately connected with their genesis.

Although an extremely rare metal, columbium exists as the pentoxide in a considerable number of minerals, in some of which—such as pyrochlore and columbite—it may be regarded as the essential constituent, while, in others, although practically always present, its proportion varies from a mere trace up to an amount which justifies its being considered as the principal oxide.

Columbium occurs in minerals only as the pentoxide Cb_2O_5, in combination with a base, the columbium in the few minerals (such as wöhlerite) which contain silica, being present as a silico-columbate, and never as a silicate of columbium.

A list of thirty or forty minerals in which columbium is commonly found in association with tantalum might be given, but the principal will be given in the article TANTALUM, with which metal columbium invariably occurs in nature. From the technical point of view, the principal columbium minerals are those which consist essentially of columbates of iron, manganese, and lime, zirconia and metals of the cerium group being also usually present in, or at any rate intimately associated with, such minerals as contain lime.

The mineral richest in columbium is *pyrochlore*, a columbate of lime containing titanium, cerium, and thorium, together with other alkaline earths and alkali bases and some fluorine. The most important mineral, however, is the columbate of iron and manganese known as *columbite* or *niobite*, in which the Cb_2O_5 may even exceed 78 p.c., a condition nearly reached by certain specimens occurring in the cryolite of Arsukfiord (Greenland).

The columbium is always partly replaced by tantalum, the proportion of which may vary from a trace through all gradations, until the mineral merges into tantalite which is isomorphous with columbite, and which occurs in much larger quantity and furnishes the bulk of the tantalum of commerce and, as a by-product, of the columbium. These two minerals are found in alluvial deposits with cassiterite and wolfram, and in isolated masses left by the denudation of

intrusions in pegmatites, &c., at Greenbushes and elsewhere in Western Australia, in Colorado (Cañon City), Dakota (Black Hills), North Carolina and other districts of the United States, and in Sweden, Norway, Greenland, Madagascar, Rhodesia, and many other districts. They may be considered to possess the general formula $(FeMn)O(CbTa)_2O_5$, the relative proportions of ferrous and manganous oxides varying within extremely wide limits.

New deposits are constantly being discovered, and columbium, like many others of the rare metals for which a demand now exists, will doubtless be found to occur in much larger quantities than is generally believed.

Amounts, far in excess of present requirements, are obtainable as by-products from the preparation of the rare earths employed for incandescent mantles, from tin and wolfram ores, and from the heavy waste material obtained in the dressing of cryolite.

Metallic columbium may be prepared by passing a mixture of the vapour of the pentachloride and hydrogen through a red-hot tube (Roscoe); by electrolysis of the oxyfluoride; in a less pure condition, by heating the pentoxide with carbon in the electric furnace (Moissan); by the alumino-thermic process, and by the method of von Bolton, introduced with a view to the manufacture of metal filament lamps, before tantalum came into use. In this process, the pentoxide is mixed with paraffin and formed into threads which are heated *in vacuô* to a temperature of over 1900° by passage of an electric current.

By the alumino-thermic reaction, von Bolton has obtained columbium containing about 3 p.c. of aluminium which can be driven off with other impurities by prolonged heating *in vacuô* in the electric furnace. The purest columbium hitherto prepared in bulk is said to have been thus obtained. Like tantalum, it can also be obtained by reduction of the fluoride K_2CbF_7 with potassium, as a black powder from which the residual hydrogen may be expelled by shaping it into small cylinders and melting *in vacuô* in an electric furnace.

Although the most important use of tantalum is for manufacture of electric lamps, in which case it requires to be separated from columbium, the amount actually consumed for the purpose is extremely small. The standard tantalum lamp, introduced in 1904, contained only one twenty-thousandth of a pound of tantalum, and those now manufactured contain much less.

The method employed for the separation of columbium from tantalum in the preparation of the latter element for electric lamp filaments probably depends essentially upon a fractional crystallisation of the mixed double fluorides of potassium with tantalum, columbium, and titanium.

Metallic columbium melts at 1950°, and has a sp.gr. of 12·7, and an electrical resistance of 0·1870 ohm for a wire 1 metre long by 1 mm. diameter. It is less malleable or ductile than tantalum, but the rolled metal has a hardness greater than that of wrought iron, and may be welded at a red heat.

Although the powdered metal oxidises rapidly when heated in air, the rolled or cast

metal is but little affected, as a protective coating of oxide rapidly forms. It is practically unaffected by an acid except hydrofluoric acid, or by solution of the alkalis, but is rapidly attacked by fused alkalis or alkaline nitrates.

It combines with carbon when heated, and at dull redness rapidly absorbs hydrogen or nitrogen and becomes brittle, the hydride and nitride respectively being apparently formed.

It reacts violently when heated with sulphur or selenium, and forms the volatile pentachloride when heated to redness in chlorine.

It does not form an amalgam with mercury, but alloys with many other metals and in all proportions with iron.

The compounds of columbium have not yet been applied commercially, but the pentoxide, generally known as columbic acid, and the fluorides, especially the double fluoride with potassium $2KF \cdot CbF_5$ are of interest in connection with the preparation of the pure compounds or metal from minerals.

For methods of analysing columbites and tantalites, and of estimating columbium in presence of tantalum, see G. Chesneau (Compt. rend. 1909, 149, 1132; J. Soc. Chem. Ind. 1910, 29, 93), J. Moir (J Chem Met and Min. Soc. S. Africa, 1916, 16, 189; J. Soc Chem Ind. 1916, 35, 637), Giles (Chem. News, 1909, 99, 1), Simpson (Chem. News, 1909, 99, 243), Metzger and Taylor (Zeitsch. anorg Chem. 1909, 62, 383), Weiss and Landecker (Zeitsch. anorg. Chem. 1909, 64, 65), cf. Foote and Langley (Amer. J. Sci. 1910, [iv.] 30, 401), cf. Hauser and Lewite (Zeitsch angew. Chem. 1912, 25, 100), Meimberg (Zeitsch angew. Chem 1913, 26, 83), Meimberg and Wintzer (Zeitsch. angew. Chem. 1913, 26, 157), Levig (Analyst, 1915, 40, 204)

For a method of estimating columbium and tantalum based on the difference between the densities of the oxides of columbium (4·552) and tantalum (8·716), see Foote and Langley (Amer. J. Sci 1910, [iv.] 30, 393), see also Ruff and Schiller (Zeitsch. anorg. Chem 1911, 72, 329).   G. T. H.

COMPOUNDS OF COLUMBIUM.

Columbium dioxide CbO or Cb_2O_2, formed by heating potassium columbium oxyfluoride with sodium, is a white powder, which burns when heated in the air, forming the pentoxide. In chlorine it ignites, forming the oxychloride $CbOCl_3$. Is soluble in hydrochloric acid with evolution of hydrogen.

Columbium tetroxide CbO_2 or Cb_2O_4, a black powder, formed by heating the pentoxide in hydrogen, or with magnesium. Burns when heated in the air to redness.

Columbium pentoxide Cb_2O_5, a white infusible powder of sp.gr. 4·53–4·568 (4·8 Balke and Smith).

Columbic acid $HCbO_3$, a white powder formed by decomposing the oxychloride or pentachloride with water. Slightly soluble in hot hydrochloric acid. Yields the pentoxide when strongly heated. *Potassium hexacolumbate* $K_2Cb_6O_{16},6H_2O$, formed by fusing the pentoxide with potassium carbonate. Large monoclinic crystals, effloresing on exposure to dry air.

Other potassium columbates are $K_8Cb_6O_{19},13H_2O$; $2K_2Cb_4O_{11},11H_2O$; $K_4Cb_2O_7,11H_2O$. *Sodium columbate* $7Na_2O,6Cb_2O_5,32H_2O$ (Bedford, J. Amer. Chem. Soc. 1904, 26, 1235); *Sodium metacolumbate* $Na_2O,Cb_2O_5,7H_2O$ (Balke and Smith, J. Amer. Chem. Soc. 1908, 30, 1637). For the composition of other columbates, see Balke and Smith (l.c.).

Percolumbic acid $HCbO_4$, an amorphous yellow powder, obtained by treating columbic acid with hydrogen peroxide. Is decomposed on warming with sulphuric acid. *Potassium percolumbate* or *pyrocolumbate* $K_4Cb_2O_{11},3H_2O$, formed by mixing hydrogen peroxide with a solution of potassium columbate and adding alcohol. Decomposed by water. Yields hydrogen peroxide and ozone with concentrated sulphuric acid For other percolumbates, see Balke and Smith (l.c.).

For the hydrosols of columbic acid see Hauser and Lewike (Zeitsch. angew. Chem. 1912, 25, 100).

For the electrolytic reduction of columbic acid and its salts, see Ott (Zeitsch. Elektrochem. 1912, 18, 349).

When columbic acid is dissolved in concentrated sulphuric acid, the solution diluted, and then reduced with zinc, an indigo-blue solution is obtained which reduces a solution of copper sulphate to metallic copper; the solution is thus more strongly reducing than one containing tervalent titanium.

Columbium pentafluoride CbF_5, colourless, strongly refractive monoclinic prisms, $D^{18} 3·293$; m p 75·5° (corr.); b p. 217°–220°/760 mm. (corr.) Obtained by the action of fluorine on columbium. Very hygroscopic; readily soluble in water. Solution precipitates columbic acid on addition of ammonia or sodium hydroxide (Ruff and Schiller, Ber 1908, 42, 492).

Columbium oxyfluoride $CbOF_3$ forms double salts with other metallic fluorides, of which the alkaline salts have been investigated by Marignac.

Columbium trichloride $CbCl_3$, a non-volatile, non-deliquescent crystalline substance resembling iodine, forming long dichroic needles. Oxidised on exposure to air, and yielding columbium oxychloride $CbOCl_3$, and carbon monoxide when heated in carbon dioxide (Roscoe).

Columbium pentachloride $CbCl_5$, yellow needles, obtained by heating columbium pentoxide mixed with charcoal in a stream of chlorine. Also formed by heating the pentoxide with sulphur monochloride S_2Cl_2; or, together with the oxychloride, by heating the pentoxide with carbon tetrachloride; m.p. 194°; b.p. 240·5°; sp.gr. 2·73–2·77. Gives a normal vapour density. Soluble in carbon tetrachloride, chloroform, and alcohol. Its solution in hydrochloric acid gelatinises, and on addition of water, forms columbic acid. On reduction with sodium amalgam gives *chlorocolumbium chloride* $(Cb_6Cl_{12})Cl_2,7H_2O$, black, shining crystals, forming an olive-green powder, insoluble in cold water, but soluble in hot water to an olive-green solution. Only two of the chlorine atoms are ionic. When treated with the equivalent amount of sodium hydroxide, *chlorocolumbium hydroxide* $(Cb_6Cl_{12})(OH)_2,8H_2O$ is formed as a black microcrystalline precipitate, and

from this the *bromide* $(Cb_6Cl_{12})Br_2,7H_2O$ is obtained. The hydroxide is soluble in excess of sodium hydroxide, and from the solution excess of concentrated hydrochloric acid precipitates a brown powder $C_6H_{14},9H_2O$ (Harned, J. Amer. Chem. Soc. 1913, 35, 1078).

Reduction of a solution of columbium pentachloride at a platinum cathode gives a blue solution, which is of a colloidal character; with gold chloride it gives a magnificent purple liquid, from which, on boiling, a purple precipitate deposits. This precipitate is similar to purple of Cassius; it colours glass a violet-red (Stähler, Ber. 1914. 47, 841).

Columbium oxybromide $CbOBr_3$ and **pentabromide** $CbBr_5$ also exist, and an iodide has been formed (Barr, J. Amer. Chem. Soc. 1908, 30, 1668).

Columbium sulphides CbS_2 and Cb_2S_5, corresponding to the oxides, have been prepared (Biltz and Gonder, Ber. 1907, 40, 49, 63).

Columbium oxysulphide $CbOS_1$, a black crystalline powder formed by heating the pentoxide in the vapour of carbon disulphide mixed with carbon dioxide.

Columbium nitride Cb_3N_5. A yellow powder formed by heating columbium in nitrogen (Moissan, Compt. rend 1901, 133, 20; Muthman, Weiss and Reidelbauch, Annalen, 1907, 335, 58).

The spectrum of columbium contains thirty-one more or less complete groups of five lines showing wave-number differences equal to $720\cdot25$, $1027\cdot02$, $355\cdot19$, and $303\cdot29$ respectively (*cf.* Siegbahn and Froman, Ann. Physik. 1916, [iv.] 49, 611).

For arc spectrum of columbium, *see* Hildebrand (J. Amer. Chem. Soc. 1908, 30, 1672).

For the magnetic resolution of the spectrum lines of columbium, *see* Jack (Proc. Roy. Irish Acad. 1912, A, 30, 42).

COLZA OIL *v.* RAPE OIL.

COMENAMINIC ACID *v.* BONE OIL.

COMMON CAMPHOR *v.* CAMPHORS.

CONCRETE *v.* CEMENT.

CONDENSERS. A condenser is an apparatus in which the vapour of a liquid may be cooled down to a temperature below that at which it is converted into the liquid state under the prevailing pressure. The condensation of the vapour is usually effected by bringing it into contact with a cold surface, to which it imparts its heat, suitable arrangement being made for conveying away this heat from the cooling surface. Although air cooling is sometimes depended upon for this latter purpose, the arrangement usually adopted consists in causing a stream of cold liquid (water in the majority of cases) to circulate over the exterior of the condensing chamber. The following points should be considered in the designing of an efficient condenser :—

(*a*) The cooling surface must be made of material upon which the vapour has no chemical action, and should be capable of withstanding repeated variations of temperature without fracture.

(*b*) The area of cooling surface should be as great as possible, without making the apparatus unduly large and heavy.

(*c*) The material should preferably have a high specific heat, so that its rise in temperature may be kept within reasonable limits; and it should have a high thermal conductivity, in order that the heat it absorbs may be rapidly carried away.

(*d*) The design should be such as to admit of the condenser being readily cleansed.

It is not possible to obtain materials entirely satisfactory in each of the above respects, and so in practice the materials employed are those which combine cheapness with reasonable satisfaction in the foregoing particulars. For laboratory apparatus, the material commonly used is glass; metals (block tin, copper, &c.) are less often employed, except for constructing fairly large pieces of apparatus; of recent years, silica has found a limited use.

Condensers are used in two different kinds of operations : (1) for condensing vapours in distillation processes, in which case a still is attached to the upper end and a suitable receiver to the lower end; and (2) as 'reflux' apparatus in cases where it is necessary to boil a liquid for some time without sensible loss through evaporation; the vessel containing the boiling liquid is then attached to the lower end of the condenser and the condensed vapours flow back into the vessel. A number of condensers described below are specially designed for this purpose.

The simplest type of condenser is the familiar form devised by Weigel in 1771, but usually known as Liebig's condenser. It consists simply of a straight cylindrical glass tube, in which the vapour is condensed. The upper end is widened out slightly to facilitate connection with the still, and its lower end is cut off obliquely; a cylindrical glass jacket is slipped over the greater portion of the length of the tube, and through it, by appropriate entrance and exit tubes, cold water is circulated in an upward direction, so that the vapours passing down the inner condenser tube encounter a surface the temperature of which continuously falls in the direction of the receiver. This type of condenser admits of considerable variation and modification in the precise details of construction ; thus, with a view to exposing a large cooling surface, the portion of the condenser within the jacket is sometimes made of approximately rectangular section, thus

, being broadened considerably in one direction ; in other condensers the central portion carries a series of bulbs blown on it. Cooling surface is obtained in some condensers by replacing the central portion by a closely wound glass spiral, as in Fig. 1, the water-jacket being sealed on to the condenser proper. The modified Weigel condenser, shown in Fig. 2 (Chem. Zeit. 1902, 26, 633), is arranged for use with the two limbs *a* and *c* of the inner U-tube on the same level to prevent accumulation of liquid at *b*. The inner tube is fused into the outer tube at *d*.

FIG. 1.

Glass condensers with water-jackets sealed on are restricted in their use to the condensation

of the vapours of liquids of fairly low boiling-point (below 100°), since otherwise the glass joints are liable to crack. For liquids of moderately high boiling-point (140°–200°), it
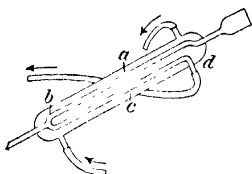

FIG. 2.

usually suffices to employ merely the inner tube of a Weigel (Liebig) condenser (air condenser).

In the reflux condensers illustrated in Figs. 3 and 4 (J. Soc. Chem. Ind. 1897, 16, 979) the relative positions of the vapour and cooling stream of water are reversed, the water entering as shown by the arrows (at *a* in Fig. 3). A large area of exposed surface is obtained in these condensers, which, it will be observed, are of the 'double-surface' type, since, in addition to the inner water-cooled surface, condensation also occurs on the outer surface, which exposes an even larger area to the cooling action of the air.

Several vertical condensers have been devised by Friedrichs in which one of the two surfaces between which the vapours condense is constructed spirally (Zeitsch. angew. Chem. 1910, 23, 2425).

A number of extremely useful, compact condensers of the 'double-surface' type have been described. The vapours are condensed in the annular space between two surfaces, both of
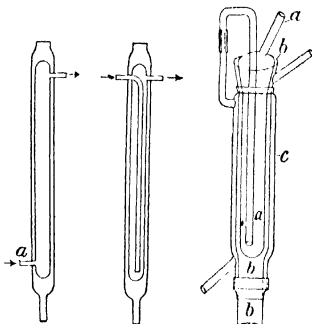

FIG. 3.   FIG. 4   FIG. 5.

which are water-cooled, the design being such that one stream of water flows in succession over each. The efficiency of this cooling process is so great that these condensers can be made quite short; they are readily fixed in a vertical position and occupy little bench space.

In the Burgess condenser (J. Soc. Chem. Ind. 1905, 24, 1190), the tubes *a* and *c* (Fig. 5) are the cooling jackets, and *b* is the condensing tube proper. Cribb's condenser (Fig. 6) consists of

two concentric tubes joined together at the top; condensation is effected in the interior chamber thus formed. Water is conveyed into the inner tube by the tube *a*; overflowing, it passes round the exterior of the outer tube and flows away by the side tube *b*. The vapour is led in through the inlet tube *c*.

Another double-surface condenser of simple construction is illustrated in the article ANALYSIS (Vol I)

The condensers illustrated in Figs. 7 and 8
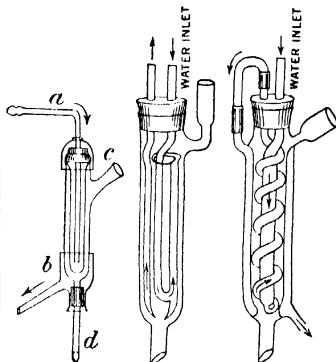

FIG. 6.   FIG. 7.   FIG. 8.

have the advantage of exposing four cooling surfaces to the vapour, and may be readily cleansed when necessary by removing the inner portions with the stopper (Chem. Zentr. 1908, ii 277).

An inquiry into the relative efficiency of laboratory reflux condensers made by Dover and Marden (J. Ind Eng. Chem 1916, 8, 834) showed that where a long condenser can be conveniently used, the Weigel is preferable, whilst the Friedrichs, or some modification of it, seems best where a short condenser must be used.

The condensers so far described are usually constructed of glass, but occasionally metals are employed. The use of *aluminium* for the inner tube of a Weigel condenser has been advocated by Norton (J. Amer. Chem. Soc. 1897, 19, 153). Many agricultural chemists, who have to deal with numerous ammonia distillations, prefer block-tin condensers; they are constructed like inverted **U**-tubes, one arm (the condenser arm) being much longer than the other and carrying a water-jacket if required, while the short arm is attached to the distilling flask. A convenient method of constructing a number of such condensers in series to be cooled by one stream of water is described in J. Amer. Chem. Soc. 1906, 28, 999.

A useful metallic condenser is the 'ball' type, used on the reflux principle in numerous experiments involving extractions with volatile solvents. Soxhlet's pattern is shown in Fig. 10, while the construction of a double-surface condenser of this pattern is sufficiently indicated in Fig. 9. Storch's metallic reflux condenser is

depicted and described in J. Soc. Chem. Ind. 1897, 16, 979.

The spiral (worm) type of condenser is frequently constructed of metal (copper) and enclosed in a metal tank which can be filled with cold water; these condensers find considerable use in small plants for preparing distilled water. For this latter purpose, a novel
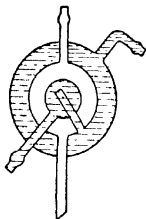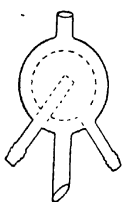

Fig. 9.   Fig. 10.

form of condenser is described in Eng. Pat. 6916, 1905, which combines efficiency with extreme simplicity of construction. The condenser, which is placed vertically above the evaporating chamber, consists of two metallic truncated cones, the lower being open at the top, while the upper is closed by a dome-shaped lid. The outer surface of the upper cone is cooled by a continuous stream of cold water, and condensation is effected upon its inner surface. The condensed vapour collects in the annular space between the two cones, and the water is continuously run off into large earthenware jars. Special apparatus, devised for preparing pure distilled water (so-called 'conductivity water') on a laboratory scale are described by Bousfield (Chem. Soc. Trans. 1905, 87, 740); Golding (J. Soc. Chem. Ind. 1906, 25, 678), and by Hartley, Campbell, and Poole (Chem. Soc. Trans. 1908, 93, 428).

Condensers of various designs are described in J. pr. Chem. [2] 34, 427; [2] 49, 44; Compt. rend. 118, 478; Ber. 1892, 24, 3950; 1895, 28, 2388; J. Soc. Chem. Ind. 1899, 18, 707; Chem. Zeit. 1902, 26, 325; 1904, 28, 598, 686; 1905, 29, 809; 1910, 34, 116; Bull. Soc. chim. 1904, 31, 1116; Chem. Zentr. 1906, ii. 993; and reflux condensers in Chem. Zeit. 1896, 20, 462; 1904, 28, 598; Bull. Soc. chim. 1901, 25, 476; 1908, 3, 855; Zeitsch. anal. Chem. 1901, 40, 769; Chem. Zentr. 1906, ii. 993; Chem. News, 1907, 95, 52; and J. Soc. Chem. Ind. 1908, 27, 962.

CONDURANGO. The dried bark of *Marsdenia condurango* (Nichols) (*Gonolobus Condurango triana*, Reichenbach; family *Asclepiadaceæ*). It is obtained from a half-climbing or prostrate shrub of Ecuador. The bark comes into commerce in quills or quilled pieces, about 10 cm. long, and rarely exceeding 2 cm. in diameter; externally brown grey, roughened, with scale like warts; internally, greyish or pale brownish-white, striate; fracture short, granular or slightly fibrous in inner layer. Taste, somewhat bitter; odour of fresh bark, aromatic.

Kubler (Arch. Pharm. 1908, 246, 620) states that the principal constituents of the bark are dextrose, other usual components of plants, the glucoside *condurangin* and a polyhydric alcohol *conduritol*. *Condurangin* $C_{40}H_{60}O_{16}$ contains two methoxyl groups, is soluble in water, alcohol, and chloroform, insoluble in ether. Dilute sulphuric acid hydrolyses it to dextrose and an amorphous powder, containing several substances; alcoholic potash yields some cinnamic acid. *Conduritol* $C_6H_{10}O_4$ crystallises from hot alcohol in colourless prisms, and yields a tribenzoyl derivative, m.p. 142°-143°. According to Carrara (Gazz. chim. ital. 21, i. 204; 22, i. 236), commercial condurangin can be separated into two parts, one insoluble and the other soluble in water. The former is a white powder, $C_{20}H_{32}O_8$, m.p. 60°-61°; and the latter a yellow substance, $C_{18}H_{24}O_7$, m.p. 134°. Hager (Handbook, 1900) has further investigated these substances and named them *a*- and *b*-condurangin; *a*-condurangin gives a green colour with Froehde's reagent (conc. sulphuric acid and molybdic acid), *b*-condurangin does not. Carrara (*l.c.*) also isolated a yellow powder, $C_{30}H_{50}O_8$, which he named *condurangsterin*, m.p. 52°. Fluckiger has isolated a small quantity of an alkaloid having a strychnine-like action. Firbas (Pharm. J. 70, 417) treats the chloroform extract of the crude glucoside with a mixture of equal volumes of sulphuric acid, hydrochloric acid, and alcohol (Lafon's reaction). On warming, a green colour is produced, changing to bluish-green on the addition of a trace of ferric chloride. Certain other glucosides give this reaction, but they are not likely to be present in the bark.

Condurango has been employed for many years in South America as an alterative in the treatment of syphilis. It is used as a stomachic, and lessens gastric catarrh and relieves the vomiting and nausea which are usually associated with carcinoma of the stomach; it is also used to lessen the pain consequent upon gastric ailments. Condurango produces in large amounts incoordination of the muscles and convulsions, which may be followed by paralysis. Dose, 1 fluid drachm of the fluid extract of condurango, or 4 fluid drachms of the wine of condurango.

There are many other varieties of condurango and marodennas. The Guayaquil condurango has several peculiarities in the wood of the bark, and has not so many medullary rays. Mexican condurangos contain a strong collenchyma next to the bark, while nearer the pith is a layer of bast fibres containing large crystals of calcium oxalate (Chem. Zeit. 11, 1601; 12, 26).

CONDY'S FLUID *v.* MANGANESE.

CONESSINE or **WRIGHTINE** $C_{24}H_{40}N_2$ exists in the bark and seeds (0·6 p.c.) of *Wrightia antidysenterica* and in *Holarrhena africana* (A. DC.), *H. congolensis* (Stapf.), and *H. antidysenterica* (Wall.). Crystals, m.p. 122° (Polstorff, Ber. 1886, 19, 78, 1682; Warnecke, *ibid.* 1886, 19, 60; Arch. Pharm. 1888, [iii.] 26, 248, 281; Pyman, Chem. Soc. Trans. 1919, 163; Giemsa and Halberkann, Arch. Pharm. 1918, 256, 201; Ulrici, Arch. Pharm. 1918, 256, 57). Soluble in acetone, from which it separates in large colourless plates, efflorescing in air; m.p. 125° (corr.) [a]−1·90°.

CONGO BLUE, -BROWNS, -CORINTH, -FAST BLUE, -ORANGE, -REDS, -RUBINE, -SKY BLUE *v.* AZO- COLOURING MATTERS.

CONHYDRINE (*Conydrine*), **Coniceine.** *See* under *Coniine*, below.

CONIFERIN *v.* GLUCOSIDES.

**CONIINE AND THE ALKALOIDS OF HEM-
LOCK.**

Coniine $C_8H_{17}N$ is one of several poisonous, volatile alkaloids found in hemlock, *Conium maculatum* (Linn.) (0·2–0·9 p.c in the not quite ripe seeds). Hemlock (*Grande ciguë*, Fr.; *Scherling*, Ger.) is a tall biennial of the temperate regions of Europe, Asia, and America, and was the essential ingredient in the potion administered to condemned criminals by the Greeks. Besides coniine, hemlock contains N-*methyl-d-coniine*, N-*methyl-l-coniine*, γ-*coniceine*, *conhydrine*, and *pseudoconhydrine*

Preparation.—Coniine is most readily separated from the crushed, unripe hemlock seeds by digesting them with water made alkaline with sodium carbonate, to decompose the coniine malate, and distilling the mixture in a current of superheated steam. The distillate contains the coniine, together with much ammonia derived from the ammonium salts present in the seeds The liquid is neutralised with hydrochloric acid and evaporated to dryness. The dry residue is extracted with absolute alcohol, when most of the ammonium chloride remains undissolved, whilst the alkaloidal hydrochlorides go into solution. If ether is added to the alcoholic solution a further quantity of ammonium chloride is separated The residue left by the evaporation of the alcoholic solution is dissolved in cold water, ether added, and the coniine liberated by the addition of potash The ethereal layer is decanted, washed, dried with potassium carbonate and distilled at a low temperature, when the coniine remains as an oily liquid. It may be purified from the accompanying conhydrine by fractional distillation ; the coniine passes over first So prepared the coniine contains γ-coniceine from which it may be freed by conversion into the hydrochlorides and extracting these when dry with acetone, in which the γ-coniceine salt is soluble and the coniine salt insoluble. For the separation of the subsidiary alkaloids by benzoylation, *see* von Braun (Ber. 1905, 38, 3108).

Properties.—Colourless, alkaline liquid, having a remarkable, penetrating odour and a burning taste ; b.p. 166°–167°, m.p. - 2° ; rel. den. 0·8626 at 0°, dextrorotatory $[a]_D = + 13·79°$.

' Coniine is slightly soluble in cold water, but less so in hot water, so that a clear, cold solution becomes turbid when warmed. It dissolves about one-quarter of its own volume of water at the ordinary temperature. When boiled with water the alkaloid distils with the steam. Coniine mixes with alcohol in all proportions, and is also readily soluble in ether, but only sparingly so in chloroform or carbon disulphide. Exposed in the air it darkens and slowly resinifies. When administered internally coniine acts as a powerful poison. It is a monacidic base The ordinary salts are crystalline and soluble in water or alcohol. The hydrochloride B·HCl forms rhombic crystals and melts at 220°. The aurichloride B·HAuCl₄, m.p. 77°, forms minute yellow needles.

Reactions.– Coniine is a strong base, which

precipitates many metallic hydroxides from solutions of their salts.

It is a secondary amine. When oxidised with nitric acid it yields *normal butyric acid* among other products. When permanganate is used *a-pyridinecarboxylic acid (picolinic acid)* is obtained. On distillation with zinc-dust coniine is decomposed into hydrogen and *a-n-propylpyridine.*

Ladenburg has inferred from these and other reactions that coniine is α-propylpiperidine and has confirmed this by effecting the synthesis of the alkaloid by hydrogenating (with sodium in alcoholic solution) α-allylpyridine

$$C_5H_4N(C_3H_5)+8H=C_5H_{10}N(C_3H_7)$$
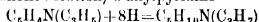
The liquid thus produced possesses all the chemical and physical properties of the natural alkaloid except one ; it is optically inactive (Ber. 1886, 19, 2579 ; 1906, 29, 2486). Ladenburg has also succeeded in resolving the inactive coniine into dextrorotatory and lævorotatory forms and has shown the dextro compound to be identical with the natural alkaloid. This was the first synthesis of a natural alkaloid.

The toxicological recognition is somewhat difficult ; in particular there are no reactions distinguishing it sharply from nicotine. Auric and platinic chlorides do not precipitate a 1 p c aqueous coniine solution, but do precipitate nicotine at much greater dilution. A trace of coniine evaporated in a desiccator with a drop of hydrochloric acid readily yields a crystalline hydrochloride, nicotine does not. Differences in odour, density, and solubility in water may also be used.

N-**Methyl**-*d*-**coniine** $C_8H_{16}(CH_3)N$ is stated to occur in hemlock (*v.* Planta and Kekulé, Annalen, 1854, 89, 150), and remains with γ-coniceine when this is separated from coniine by fractional crystallisation of the acid tartrates. It has been synthesised by methylating coniine with potassium methyl sulphate (Wolffenstein, Ber. 1894, 27, 2611 ; *cf.* Passon, *ibid.* 1891, 24, 1678). It is a colourless, oily liquid, b.p. 173°–174°, closely resembling coniine.

N-**Methyl**-*l*-**coniine** was obtained by Ahrens (*ibid.* 1902, 35, 1330) from residues accumulated in the preparation of coniine.

Coniceines. This name has been applied to a series of isomeric bases, $C_8H_{15}N$, obtained in various ways from the hemlock alkaloids. Only one of them γ-*coniceine* (2-propyl-Δ′-tetrahydropyridine) occurs in hemlock and was isolated from crude coniine obtained therefrom by Wolffenstein (Ber. 1895, 28, 302) ; occasionally as much as 70 p.c. of the crude alkaloid was γ-coniceine. This base was first prepared by Hofmann by the action of alkalis on bromoconiine. It strongly resembles coniine in odour and appearance, boils at 171°–172° under 746 mm. pressure, yields crystalline salts, and furnishes coniine on reduction. It has the constitution

γ-Coniceine.   Coniine.
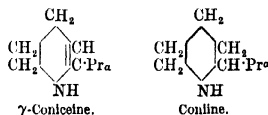
Cf. Hofmann, Ber. 1885, 18, 16, 27, 112 ; Lellmann, Annalen, 1890, 259, 127 ; Löffler and

colleagues, Ber. 1909, **42**, 94, 107, 116, 124, 948, 3420; Gabriel, *ibid.* 1909, **42**, 4059.

Conhydrine $C_2H_{17}ON$, also found in hemlock, may be separated from coniine with which it occurs either by cooling- the concentrated ethereal solution of the two alkaloids, when the conhydrine crystallises out; or it may be obtained by distilling the crude coniine, when it remains behind in the retort, if the temperature has not exceeded 180°.

Conhydrine is a crystalline, basic substance, m.p. 121°, b.p. 226°, $[\alpha]_D + 10°$. On heating with phosphorus pentoxide, or with concentrated hydrochloric acid, it furnishes a mixture of α- and β-coniceines (*see* above). According to Willstätter it is 2 : β-hydroxy-propylpiperidine (Ber. 1901, **34**, 3166; *cf.*, however, Löffler and Tschunke, *ibid.* 1909, **42**, 929).

Pseudoconhydrine $C_8H_{17}ON$, which is also found in hemlock, closely resembles conhydrine. It is a crystalline, strongly basic substance, m.p. 105°–106°; b.p. 236°. It is a secondary base and forms crystalline salts (Ladenburg and Adam, Ber. 1891, **24**, 1671). Engler and Baur regard it as 2 : α-hydroxypropylpiperi-dine (*ibid.* 1894, **27**, 1777), and Löffler has suggested that it is 4-hydroxy-2-propylpiperi-dine (*ibid.* 1909, **42**, 116). (G. B.

CONIMA RESIN, CONIMENE *v.* OLEO-RESINS.

CONQUINAMINE *v.* CINCHONA ALKALOIDS.

CONSTANTAN *v.* NICKEL.

CONVALLAMARIN, CONVALLARIA *v.* DIGI-TALIS.

CONVALLARIN $C_{34}H_{62}O_{11}$ (Walz), $C_{25}H_{40}O_{10}$ (Lindner). A glucoside contained in *Convallaria majalis* (lily of the valley). On heating with dilute sulphuric acid it is hydrolysed to a hexose and *convallaretin* $(C_{19}H_{28}O_4 ?)$, a crystalline substance which forms a stable monohydrate. It contains a benzene ring, but is free from ethylenic linkings, ketonic, and methoxyl groups, and contains two hydroxyl radicals; the two remaining oxygen atoms appear to constitute part of a carboxy-ester group (Lind-ner, Monatsh. 1915, **36**, 257). *Cf.* DIGITALIS.

CONVICINE *v.* VICINE.

CONVOLVULIN *v.* GLUCOSIDES.

COOMASSIE NAVY BLUE, -WOOL BLACKS, *v.* AZO- COLOURING MATTERS.

COPAIBA BALSAM *v.* OLEO-RESINS.

COPAIBA OIL *v.* OILS, ESSENTIAL.

COPAIVENE, COPAIVI, COPAIVIC ACID *v.* OLEO-RESINS.

COPAL *v.* RESINS.

COPAL VARNISH *v.* VARNISH.

COPALIN *v.* RESINS.

COPPER. Sym. Cu. At. wt. 63·57. Melt-ing-point in air, 1062°; in reducing atmosphere, 1084°. Specific gravity : Roberts Austen (Int. Study of Met. 1910, 15) gives 8·217 as the sp.gr. of the molten metal. Copper, deposited by electrolysis from an acid solution of copper-sulphate and not subjected to any mechanical treatment, was found to have sp.gr. of 8·9544 at 15·5° in air (Watson, J. Soc. Chem. Ind. 2, 153).

Commercial · copper, prepared in the usual way, is never pure, and the examination of the fractured surface of a cast ingot of copper shows a minutely vesicular structure. On this account the density of such metal is less than the same sample of metal after it has been sub-jected to a compressing mechanical treatment, and varies from 8·2 to 8·6

Colour.—Copper has a characteristic red colour which, in a fractured surface of worked metal, may be described as salmon-red.

Lustre.—A smooth cut or polished surface shows a bright metallic lustre which, however, soon tarnishes.

Crystalline system.—Copper crystallises in the cubical system.

Ores of copper. The following minerals are those from which copper is extracted on a com-mercial scale : native copper, cuprite, mela-conite, malachite, azurite, chrysocolla, ataca-mite, chalcocite, bornite, chalcopyrite, fahl ore.

The importance of the several species in the above list as ores of copper varies very much with the locality. Thus, while native copper is the chief ore in the Lake Superior district of North America, and atacamite in one or two localities in Chile, they would in other localities, and generally, be looked upon as rather rare, especially so in the case of the last species men-tioned. So also in the case of malachite ; this species, as an ore of copper, is seldom met with except in small quantities in the upper and oxidised portions of some copper lodes ; yet in the case of the once celebrated Burra Burra mine in Australia, and at Nischne-Tagilsk in Russia, it formed the bulk of the ore produced, and is also the chief ore in the Tanganyika district, Africa.

Generally, in a copper-mining district, all the oxidised species mentioned above occur in varying proportions, but as depth is attained, and almost invariably at or about the level at which water is reached, the copper-bearing minerals change and the oxidised species give place to the richer sulphide species, and these finally to chalcopyrite intimately mixed with varying proportions of pyrite. The inter-mingling of the two species last mentioned is frequently so intimate that it is not easy to distinguish the component minerals or to separate them. Chalcopyrite thus diluted down, as it were, with one or more of the minerals—pyrite, pyrrotite, &c —forms the ore from which the greater proportion of the world's copper supply is derived and the bulk of the material treated at the smelting works generally. Such ore frequently contains appreciable quantities of gold and silver. The silver is frequently carried by intermixed fahl ore, but also, in many instances, by the pyritic mixture in which dis-tinct silver-bearing minerals are not observable.

As by far the larger proportion of ore pre-sented for metallurgical treatment is of the nature indicated above, viz. chalcopyrite mixed with varying quantities of the pyrite family of minerals, it will best serve the purpose of this article if the methods adopted for the extraction of copper from this material are first considered. The ores treated generally contain only small percentages of copper, frequently not more than 1 p.c.

The elimination of the several elements in the ore and the final production of the copper in the metallic state, are effected by two distinct series of chemical operations. One of these—the most important, because of its very general application—treats the ore by smelting, and

causes the necessary reactions to take place while the material is in a molten condition. The other—of limited application—treats the material in the wet condition, and causes the necessary reactions to take place in solutions.

These two distinctly different methods of procedure may be distinguished as (a) dry methods, and (b) wet methods.

Dry methods. The object which the smelter keeps in view in the first stages of the processes is to concentrate the copper contained in the ore in as small a quantity of material as may be economical. For this purpose, the product known as 'matte' or 'regulus' is universally selected. This consists of cuprous sulphide Cu_2S and iron sulphide FeS in varying proportions, together with sulphides of certain other metallic elements. The whole of the copper contained in the ore thus passes into the matte, while the silica combines with iron oxide and earthy bases, if present, and forms the slag. The slag separates easily from the matte, owing to its lower specific gravity, and is thrown away. Having thus concentrated the copper into regulus, or matte, the next stage of the process concerns itself with the decomposition of this matte in such manner as to eliminate the iron and sulphur and, as far as possible, other metallic elements which may be present and to yield the copper in the metallic state

The final process consists in refining the copper produced as above; or, in other words, removing, as far as practicable, the small quantities of such elements as may still be present in the product of the preceding operation which would injuriously affect the copper for manufacturing purposes

The treatment of the ore involves, therefore, three distinct operations :—

I. Smelting the ore with the production of matte and slag.

II. Treatment of the matte for the production of crude copper.

III. Refining.

The methods and the plant used for carrying out each of the three operations vary considerably, and the choice of any one depends upon local conditions, the nature of the ore as regards physical character, and the nature and quantity of the foreign elements present. It will not be possible within the limits of this article to study these considerations and the bearing they may have on the methods to be adopted; all that the space will allow of is a description of the methods as actually carried out under the most generally prevailing conditions.

I. *Smelting the ore with the production of matte and slag.*—The object of this process being the concentration of the copper in the matte, the chief considerations kept in view are the production of a matte as rich in copper, and a slag as poor in copper, as is practically and economically possible.

The grade of the matte to be produced having been decided upon, the smelter regulates this by suitably proportioning the sulphur in the ore to be treated so that there shall be sufficient to form Cu_2S with all the copper, and a further proportion to form FeS with the iron present in such quantity as will cause the matte to contain the desired percentage of copper. From these considerations it will be seen that the factor which regulates the grade of the matte is the quantity of sulphur present in the ore mixture smelted. With the class of ore under consideration, it invariably happens that the quantity of sulphur present is considerably in excess of requirements, and the production of the most suitable grade of matte necessitates the removal of this excess, which may be effected before the actual smelting of the ore is commenced. Under certain favourable conditions, however, it may be removed during the smelting process (see *Pyritic smelting*). This preliminary operation is designated 'calcining' or 'roasting.'

The process consists in subjecting the ore to a dull-red heat under oxidising conditions, so that the sulphur is caused to combine with oxygen derived from air admitted into contact with the ore with the production of sulphur dioxide, while the iron is also oxidised at the same time.

The method of carrying out this calcining process depends upon whether the ore is to be treated .

(a) In the rough—say in pieces from ¾ inch cube upwards ; or

(b) As fines or 'concentrates,' i.e. in which the particles are finely divided.

Under (a) : *The ore may be calcined by forming heaps of it in the open air* and starting the combustion by means of a small proportion of wood, the combustion being maintained by the sulphur present in the ore.

The ore may also be calcined in stalls more or less open. These consist of series of chambers in rows built back to back. The chambers are each bounded by three walls, viz back and two side walls, but are open in front and have no roofs. Small flues, opening out into the chambers, are built in the walls separating them, and these flues connect with a larger flue in the central division wall between the two rows, and these again connect with a chimney stack.

The ore is charged into these open chambers on to a layer of wood , when filled up, the wood is fired and combustion extends to the ore itself in the same way as in the case of the heaps. The gases produced in the operation are to a large extent led away by the flues in the walls above referred to. The annoyance caused by the escape of these gases at or near the ground level of the works—as is the case in open-heap roasting—is in this way to a large extent avoided.

The ore may be calcined in kilns.—These are similar to the stalls, but are generally built of much larger size, are closed in on all four sides, and are roofed over. They are provided with suitable openings in the roof through which the ore is introduced, and a doorway in the front wall (bricked up when the kiln is in operation) through which the calcined ore is removed. An outlet flue, connected to the roof or back wall, allows the gases to be conveyed to a chimney.

The ore may be calcined in 'burners.'—These are constructed and worked on very much the same lines as the 'burners' used for burning 'pyrites' at sulphuric acid works. In this plant, a number of closed cells or 'burners' are built in rows, back to back. Each cell is roofed in and connects at the back with a

central flue common to all the cells, by which the gases are led to the acid chambers. In the roof of each cell is an opening through which the ore can be charged from a hopper placed above. In this class of plant, the ore does not rest on the floor as it does in each of the cases previously considered, but upon a series of square bars suitably spaced. Below these bars is an enclosed space with suitable door through which the calcined ore is removed and by means of which the air supply is regulated.

In operating this plant, the cell having been brought up to a good red heat by the combustion of wood or other suitable fuel, ore in small quantities is gradually added as combustion proceeds, until the burner is full. At suitable intervals, a small quantity of the calcined ore is removed from the bottom of the burner and a corresponding fresh supply of ore is added through the opening in the roof. In this way, the operation of the burner is rendered continuous, and no fresh extraneous fuel is required after the first starting of the fire.

In all the methods of treatment described under (a), it is essential that proper care be taken to prevent the temperature reaching anything like melting-point. If the ore melts or sinters together, calcination is delayed owing to the reduced surface on which oxidation can take place. Further, in the case of such sintered or melted material, difficulties are created in working the process. In the case of heap roasting and also in the stalls and kilns, the formation of large masses of sintered or melted ore introduces undesirable irregularities in the air current through the mass of ore under treatment, and
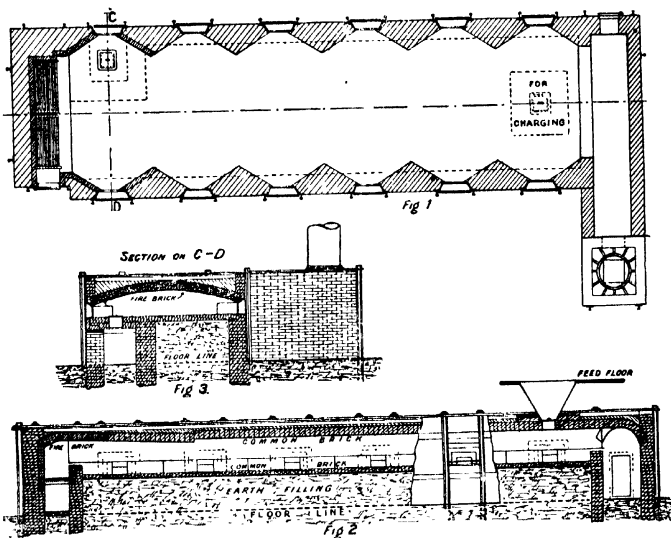
FIGS. 1, 2, AND 3.

causes trouble when the ore is removed. In the burners, the formation of sintered masses of ore must be avoided, as such masses would have to be broken up in the burner with suitable tools before it could be made to pass out between the grate bars.

Under (b) : *The ore may be calcined in hand calciners or mechanical calciners.*—The former are not much used at the present time, as the necessary labour is effectually replaced by mechanical appliances. The hand calciner, which was universally used some years ago, consisted of a long flat bedded reverberatory furnace, with the usual fire box at one end and the outlet flue for the exit of the gases at the opposite end (Figs. 1, 2, and 3). The ore was dropped from a hopper through an opening in the roof on to the bed at the flue end of the furnace, where it was spread out by means of suitable tools worked by men at both sides of the furnace, operating through doors in the side walls.

The conditions in the furnace were intensely oxidising, and it was necessary to stir the ore frequently to prevent it sintering. In the process of stirring, the ore was turned over and moved towards the fire end, thus making room for a fresh charge from the feed hopper. This process of stirring and moving the ore forward towards the fire end was continued until the ore reached close up to the fire box, at which point it was discharged through openings in the bed of the furnace into vaults, or chambers, constructed below, from which—when sufficiently cool—it was removed. The labour required on these furnaces was very heavy and the output small, and, except in unimportant installations, they have given way to furnaces in which the

ore is stirred, moved forward, and discharged by mechanical means operated by power. It will be impossible within the limits of this article to describe the many furnaces of this type which have been introduced, and it will suffice to describe one or two which will serve as examples of the class of plant employed.

The McDougall furnace (Fig. 4).—This is very largely used, and consists of a series of flat circular superimposed firebrick hearths, enclosed in a brick-lined cylinder of steel plate. An iron shaft passes centrally up the cylinder through openings in the several hearths, and is
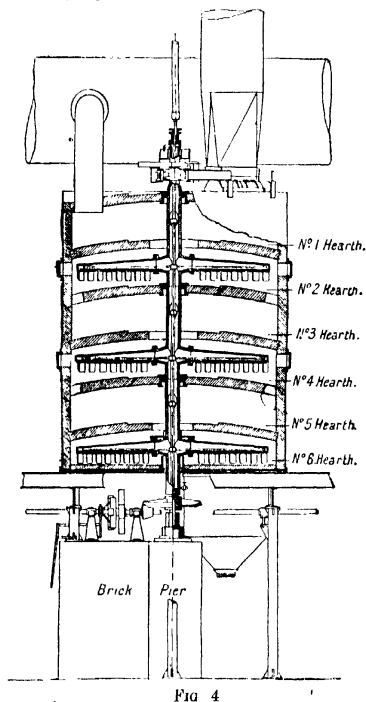

N° 1 Hearth.

N° 2 Hearth.

lᵗ°3 Hearth.

N° 4 Hearth.

N° 5 Hearth.

N° 6.Hearth.

Brick   Pier

FIG 4

(From Gowland's Metallurgy. Charles Griffin & Co., Ltd)

caused to revolve by suitable gearing attached either to its upper or lower end. This shaft may be made hollow and cooled by air or water circulation.

One or more iron arms are attached to this shaft above each bed. The arms extend from the shaft to the periphery of the circular beds, and have attached to them a series of iron plates or ploughs set at a slight angle to the arm. The ore is fed from a hopper on to the top bed near the centre, and the angle of the ploughs is such that, as the arms revolve, they not only turn the ore over, but gradually move it from the centre to the edge of the bed. At one point in the edge of the bed is an opening through which the ore

falls on to the second bed. On this bed the ploughs are so set on the arms that the ore travels in the reverse direction and is drawn to the centre of the bed. Here it discharges on to the third bed ; and so on until it escapes at the bottom of the furnace. The openings through which the ore falls from one bed to the other also serve as flues through which the gases pass upwards through the furnace, finally escaping through a flue above the top bed.

Attached to the lowest bed is a fire box by which the furnace is heated up in order to start it ; but, after being once started, little or no fuel is required, as the oxidation of the ore provides sufficient heat throughout the apparatus.

The straight-hearth mechanical furnace.—This type of furnace passes under various distinctive names, according to the several methods adopted for operating the ploughs, and slight modifications in the construction. One such furnace consists of a flat bed about 100 feet long covered with an arch. At one end is the inlet for the ore, and at the opposite end is the outlet. At the ore inlet end is the flue for carrying off the gases, and at the opposite end, but to one side, is a fire box with the inlet to the furnace constructed in the roof of the latter. Other similar fire boxes—one or two in number—are placed at intervals along the length of the furnace. A channel is constructed in the side walls of the furnace and in these a rail is laid. A suitable carriage with wheels resting on the rails stretches from one side of the furnace to the other, and the bearings pass through slots in the two side walls and are carried by the wheels above referred to. To this carriage, suitable ploughs are attached in such manner that, in the course of its travel from one end of the furnace to the other, the ploughs turn the ore over and also move it forward. The carriage is moved by a pair of chains or ropes travelling in the channels formed in the side walls, and at the two ends of the furnace these chains or ropes are carried round wheels sufficiently large in diameter to lead them back under the furnace, thus making them continuous. One pair of these wheels is driven by suitable gearing, thus causing the pair of ropes or chains—and with them the carriage —to travel the whole length of the bed of the furnace, returning through the tunnel under the bed, where rails are laid for supporting the carriage. Two or more such carriages are attached to the ropes, or chains, at equal distances apart. The ore is fed mechanically on to the bed at intervals just as a carriage is about to enter, and the ore is spread, turned over, and moved forward gradually from one end of the furnace to the other. Each time a carriage emerges from the furnace, it draws with it a quantity of calcined ore. The carriage and its attached ploughs are cooled during the passage through the tunnel. The ends of the furnace are closed by light iron doors which hang down vertically and are automatically opened by the passage of the carriage and close themselves as soon as the carriage has passed.

There is yet another method of removing the excess sulphur which is sometimes used, known as ' pot roasting,' or ' blast roasting.' This method of calcining is advantageously applied to concentrates and fines, and, while it eliminates the sulphur, the heat attained is at the same

time sufficiently intense towards the end of the process to cause the ore to partially melt or sinter together, forming a mass which requires to be broken up before it can be treated in the smelting furnace. The process is carried out in a similar manner to that used in the treatment of lead ores, but is not very extensively used in the metallurgy of copper.

After the sulphur in the ore mixture has been reduced to the requisite amount, the ore is ready to be smelted. For this operation one of two distinctly different types of furnace are used ; these are :

    (1) Blast furnace.   (2) Reverberatory furnace.

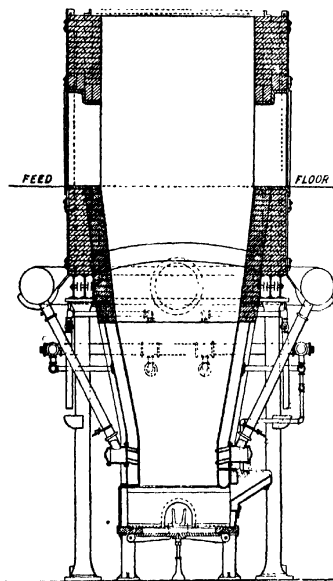The choice between these two methods of carrying on the smelting operation depends on a

FIG. 5.

variety of circumstances, all of which must have proper consideration, but the following are the chief points, viz. : If the ore is to be smelted in the state of fines or concentrates, it is unsuitable for blast-furnace treatment, while it is eminently suitable for the reverberatory furnace. On the other hand, rough ore is unsuitable for reverberatory-furnace smelting.

Blast-furnace smelting.—The furnace used may be built of brick, but is more generally, nowadays, constructed with water-cooled walls of steel plate (Fig. 5), each section of which is termed a jacket. In the smaller furnaces the horizontal section is circular, but in the ordinary sized and larger furnaces the section is always rectangular. As the working of this type of furnace is—as its name implies—dependent upon an air blast projected into the interior,

the width of the furnace is limited by the strength of the blast which is required to penetrate the charge from the sides to the centre of the furnace, while the length of the furnace is only limited by the capacity required. The increase in length is obtained by clamping together two or more of the jackets on each side, thus extending the longer axis of the furnace.

The jackets stand on a thick cast-iron plate carried on iron supports. In some cases these jackets are only used in the lower part of the furnace, all the upper part being constructed of brick, but the brickwork may, in certain cases, be advantageously replaced with a second tier of jackets, reaching up to the feed floor. Above the feed floor the furnace is continued in the form of a covered-in brick chamber with lifting doors at each side and an outlet in the roof of the chamber, connecting, by means of a suitable iron flue, to the general flue system of the works. Through the doors the charge, consisting of a proper mixture of ore—either raw and calcined, or partially calcined ore—is introduced. To this ore mixture there is also added such flux, either limestone or silicious material, and the necessary amount of coke as is required to form a suitable smelting mixture. As previously indicated, the object of this is to produce a matte of the desired grade and a slag which shall be as free from copper as possible and which shall be of such fusibility as to flow readily from the furnace. On the lower or working floor, the furnace is provided, either at the ends or sides, with one or more spouts through which the molten products of the smelting operation flow. Except in very large furnaces, only one such spout is used at a time, and if more than one is fitted, it is with the object of having one in reserve in case of a stoppage to the one in use.

The side jackets of the furnace are provided with circular openings (tuyères) passing from the outer to the inner surface. When the jackets are set up, these tuyères form a horizontal line of openings on each side of the furnace. The blast is brought down from the air main by light iron piping to the tuyères, and through these it passes to the interior of the furnace.

The blast, at a pressure of 10–42 oz. per square inch, is generated by a suitable blowing machine, which must be of the positive, and not the fan, type. A plentiful supply of water is circulated through all the jackets, and the overflow pipes from these, carrying away the hot water, discharge into sinks or launders.

The products of the smelting operation performed in this furnace flow out through the spout above described into the settler. In the case of small furnaces this is a square cast-iron vessel open at the top and mounted on wheels to allow of easy replacement. It is furnished with a cast-iron spout at its upper edge through which the slag overflows, and is provided with a tap hole near the bottom from which the matte is tapped from time to time. In the case of larger furnaces for this form of settler, there is substituted a circular tank, formed of steel plates lined with refractory material, placed permanently in position under the spout of the furnace. This form of settler may be 10 or more feet in diameter, and, like the smaller

pattern mentioned above, is provided with a slag spout near the top and a tap hole near the bottom.

In the settler, a thorough separation of the slag and matte takes place : the matte, having the higher specific gravity, falling to the bottom of the vessel and the lighter slag rising to the top, where it overflows through the spout into suitable pots provided for its removal to the slag dump. From time to time the matte is tapped off through the tap hole at the bottom of the settler. The working of this type of furnace proceeds continuously, fresh ore charges being dumped in at the top at short intervals, while a constant flow of slag and matte passes out through the spout.

Reverberatory-furnace smelting – The furnace used is essentially different both in construction and method of working from the one previously described. In the blast furnace, the fuel—coke —is burnt in contact with the materials to be smelted, and the intense heat required for the operation is obtained by urging the combustion of the fuel by means of an air blast In the reverberatory furnace the material to be smelted occupies one compartment of the furnace, while the fuel coal or wood—is burnt in another. The draught required for the combustion of the fuel is quite moderate, and is obtained by a chimney of suitable height and area. The use of pulverised coal has recently

been introduced in reverberatory furnace practice, with gratifying results, from a fuel economy point of view. The working bed of the furnace in plan is a parallelogram (Fig. 6) with rounded corners. At one end, and separated from it by a low partition, is the fire box, in which the fuel is consumed. At the opposite end is the outlet flue connecting with the chimney. A brick arch extends from the back wall of the fire box to the flue. This arches the furnace across from one side wall to side wall, and is constructed with a fall from the fire-box end to the flue end of the furnace. The partition, or bridge, as it is termed, to which reference is made above as separating the working bed from the fire box, reaches to such a height above the bed that an opening is left between its top surface and the roof of the furnace. Through this opening above the bridge, the flame from the burning fuel passes over the bed on its way to the outlet flue The side walls of the furnace are pierced with a number of openings used in working the furnace for spreading the ore charge, drawing off the slag, &c , and one opening is cut down to the lowest point of the bed for tapping the matte

The furnace walls and roof are constructed of highly refractory bricks with an outside casing of ordinary bricks, and the whole is bound together
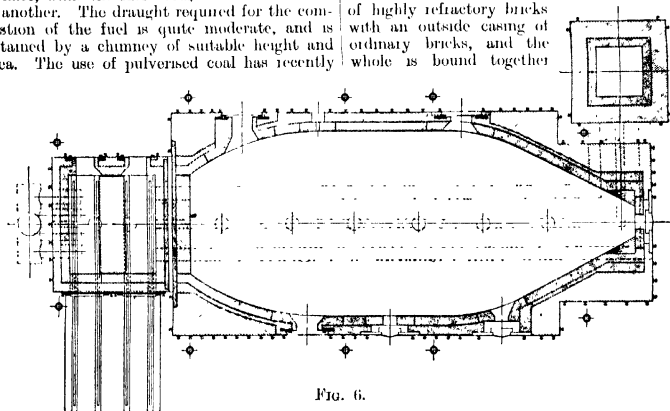

FIG. 6.

with steel girders placed vertically and tied together from one side to the other by iron tie rods. The working bottom is variously constructed. It may be formed of highly refractory bricks, or of silicious sand or crushed quartz.

The charging of this furnace takes place through one or more openings in the roof from hoppers supported above Assuming that the furnace is heated up to the required temperature, a charge of ore mixture is dropped from the hoppers above through the openings in the roof. This is then spread over the bed by means of suitable tools operated by men working through the side and front doors. When this operation is completed, the doors are closed and the fire attended to so as to raise the temperature of the furnace as rapidly as possible to full heat. The charge is occasionally stirred, if necessary, to remove any agglomerated masses from the bottom of the furnace, and

finally, a molten bath is obtained composed of two distinct layers—the matte forming the bottom layer, and the slag floating upon it. When this stage is reached, another charge may be dropped and treated in the same way ; and this may be repeated from time to time until the furnace is full of molten slag and matte. A side door and end door are opened and the slag allowed to run off, and towards the end, this is drawn off by means of tools handled by the furnace-men until nearly all the slag has been removed. The tap hole is then carefully opened, and this being at the bottom of the furnace, the matte flows through it and is led by a launder into a ladle or into moulds placed on the floor to receive it. When nearly all the matte has been run off, the tap hole is again closed and made secure, fresh charges are dropped in, and the operations repeated.

The slag may be received in ladles mounted

on wheels, and in these may be removed to the dump, run into a stream of water and thus granulated and removed ; or it may be run into sand moulds formed on the floor of the furnace house, and, when cool, broken up and removed to the dump.

The object attained in this operation in the reverberatory furnace is the same as with the blast furnace, viz. the production of the proper grade matte and a slag of easy fusibility reasonably free from copper.

Pyritic smelting.—This method of working secures in one operation what, in the preceding descriptions, is attained in two processes carried on in separate appliances. It has been shown that in order to produce a proper grade of matte from cupriferous iron pyrite, a certain proportion of sulphur must be oxidised to sulphur dioxide, and that, accompanying this action, a portion of the iron sulphide must also be oxidised. It has also been shown that, in ordinary working, this preliminary treatment and the actual smelting of the ore are carried out as two distinct operations. It has also been indicated that in the smelting operation proper, the high temperature necessary is obtained by the combustion of carbonaceous fuel. In pyritic smelting, the two processes referred to above are carried out as one operation in one furnace, and the high temperature necessary is derived from the rapid oxidation of the sulphur and iron (chiefly the latter) contained in the ore itself. While this method of working is of the highest importance from an economical point of view, it is of somewhat limited application, owing to the fact that comparatively few mines produce ore which—as regards its physical condition and chemical constitution—is suitable for this method of treatment.

The process is carried out in blast furnaces, and for its successful operation demands a larger volume of air per unit of time than the ordinary smelting process and an ore mixture in which the pyritic material is present in fairly large pieces. The silica must be, for the most part, free silica (quartz), and not combined with earthy bases as silicates. Under these circumstances the ore may be satisfactorily smelted, producing the required matte and slag with the consumption of but 1 to 3 p.c. of coke instead of 10 to 12 p.c. used in the ordinary method of smelting. A small amount of coke is found to be desirable in order to keep the charge open.

II. *Treatment of the matte for the production of crude copper.*—It has already been pointed out that matte consists of cuprous sulphide Cu_2S, with varying proportions of iron sulphide FeS, and the carrying out of the stage which is now to be considered involves the elimination of the sulphur and iron, while the copper is left in the metallic state. The process is carried out by different methods, the chief of which will now be considered. In all of those the operation is performed in two stages, although, in some cases, these follow one immediately after the other and in the same apparatus, while in others the stages are performed as two separate operations and in two or more separate furnaces. The first stage in each case consists in the removal of the FeS with the production of Cu_2S, and the second stage treats the Cu_2S with the production of metallic copper. The carrying out of the

first stage depends upon the fact that, when matte is exposed to oxidising conditions, the iron sulphide is the first of its constituents to be decomposed, the sulphur being oxidised to sulphur dioxide. The resulting iron oxide is then caused to combine with silica, forming a slag which can be removed from the residual cuprous sulphide.

The second stage in the process depends upon one or more of the reactions represented by the following equations :—

$$Cu_2S + 2Cu_2O = 6Cu + SO_2 ;$$
$$Cu_2S + 2CuO = 4Cu + SO_2 ;$$
$$Cu_2S + CuSO_4 = 3Cu + 2SO_2 ;$$
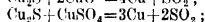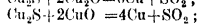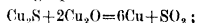
the first being the most important as representing the change which takes place in the largest proportion of the material. The reactions indicated are effected by bringing the several compounds together in a molten condition. The oxidised compounds may be added to the molten Cu_2S from outside sources or may be, and generally are, produced by the oxidation of a portion of the cuprous sulphide itself.

The reactions outlined above are, at the present day, almost always brought about by what is termed the 'converter process,' also named ' Bessemerising,' the former name derived from the designation of the vessel in which the operation is performed, viz. converter, and the latter from the name of the distinguished inventor, Sir Henry Bessemer, who had many years previously applied a similar method and plant to the production of steel from pig iron.

The converter consists essentially of a vessel formed of steel or iron plate, with a thick lining of either highly siliceous rock to which a small quantity of clay has been added, sufficient only to give the necessary coherence, or of basic material. The vessel is provided with a suitable aperture serving the purpose of a charging opening through which the matte to be operated upon is poured in a molten condition, also as an outlet through which the products of the operation are poured, as well as being an escape for the gases produced in the process. The vessel is supported on horizontal trunnions or on friction rollers, and is capable of being rotated by electric or by hydraulic power (Fig. 7). The form of the vessel is more or less cylindrical with the axis of the cylinder placed vertically or horizontally. In the case of the former, a shallow circular enclosed space, termed the air box, is attached on the outside at the bottom of the vessel. In the latter form, this air box takes the shape of a long rectangular box attached horizontally to the outside of the converter. From these boxes holes are led through the plates forming the casing of the converter, and are continued through the lining to the interior. Air, at a pressure of from 8 to 12 lbs. per square inch, is supplied to the air boxes as required, and the supply is controlled by suitable valves. Charging of the converter with matte is effected by means of a launder direct from the furnace, or settler, or by tapping these first into a steel ladle handled by an overhead crane which conveys it to the converter and pours it.

When an acid lining is used, the converter, having been lined and the lining dried by a slow fire, is placed upon the stand and connected up

to the air main A charge of molten matte is then poured in, the converter having been tilted into a suitable position for receiving it. The air being turned on, the converter is then tilted over so that the tuyères are brought beneath the surface of the matte, and the air,
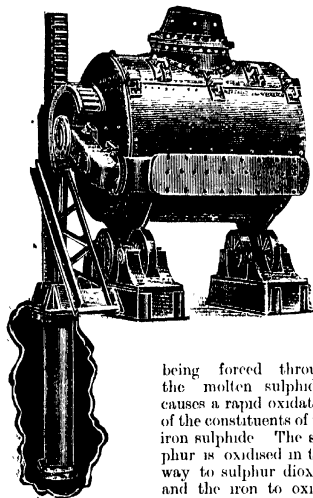

being forced through the molten sulphides, causes a rapid oxidation of the constituents of the iron sulphide The sulphur is oxidised in this way to sulphur dioxide and the iron to oxide, which is immediately converted to silicate by combination with the silica of the lining. As

FIG. 7.

the oxidation proceeds, the temperature of the charge increases and the operation is continued until practically the whole of the iron sulphide has been decomposed, and the contents of the converter consist of cuprous sulphide and slag. The converter is now turned over and the slag run off into pots or moulds, and when this is done, it is again turned into the blowing position, when the second stage of the oxidation is commenced. The passage of the air through the molten cuprous sulphide brings about the oxidation of a part of that material to cuprous oxide, which immediately reacts upon unaltered cuprous sulphide with the production, of an equivalent quantity of metallic copper, in accordance with the reactions already given. This action continues until all the cuprous sulphide has been decomposed and the contents of the converter consist of metallic copper ; any small quantity of slag which may be on the surface is removed by turning down the vessel and skimming off. The metallic copper is then poured by tilting the converter. As the slags produced in the operation contain a certain amount of copper they are resmelted in the furnace in which the matte was produced in the first place. As soon as the copper has been poured, the converter is ready to receive another charge, and the operations are repeated. When several charges, generally 5 to 10, have been put through (the number depending upon the nature of the material of which the lining is formed and

the care exercised in ramming it into place), the lining becomes too thin for further use ; the converter is therefore removed to the relining department by means of the crane, the old lining is taken out and a fresh one put in, when, after drying, it is again ready for use.

Owing to the frequency of this relining necessary in the acid converters, basic lined converters have been introduced, magnesite bricks being used for this purpose. The silica which is necessary to flux off the oxide of iron formed by the oxidation of the iron sulphide in the matte, is charged into the converter in the form of dried silicious ore. Very large basic lined converters are now being used and the method of working varies somewhat from that used in the case of acid lined converters. The copper from a previous charge having been poured, 30 to 40 tons of matte may be poured into the converter followed by about 3 tons of silicious ore which may itself be cupriferous. The blast is then put on and the converter slowly turned until the tuyères are below the level of the matte. For the first few minutes a blast pressure of only 5 lbs is used, and after the matte and silica have thoroughly intermingled, the blast pressure is increased to about 12 lbs. per square inch. When the silica has been fluxed by the iron oxide, the converter is turned down and the slag poured off. A further charge of 6 to 7 tons of matte and sufficient silicious ore are now added and the blow is resumed. This removal of slag and additions of matte and ore are continued until sufficient white metal or cuprous sulphide has accumulated in the converter to be blown to metal in the usual way.

Another method for the production of metallic copper from the matte is conducted entirely in reverberatory furnaces, and is sometimes employed where the output does not justify the more expensive converter plant previously described. In this method of working, the first stage, viz. the removal of the iron sulphide of the matte by oxidation of its constituent elements, is effected by smelting the material with a proper proportion of calcined matte together with silica sufficient to form a silicate of iron slag with the iron oxide ; or the matte may be smelted with oxidised copper ore, silica being also present. In either case, the result is that the iron sulphide is decomposed, the sulphur passing from the furnace as sulphur dioxide, and the iron forming, with the added silica, a slag, which is removed. The contents of the furnace at this stage consist chiefly of cuprous sulphide, Cu_2S. Currents of heated air are directed over the surface of the molten bath, with the resulting formation of cuprous oxide and the concurrent reaction between this and the unchanged cuprous sulphide results in the production of metallic copper, in accordance with the equations previously set out. When this reaction has extended to the whole contents of the furnace, the heat is raised and the metallic copper is tapped out into moulds.

III. *Refining.*—The method of treatment to be adopted in this operation depends upon whether (a) the copper is practically free from gold and silver and from deleterious elements ; (b) the copper contains appreciable quantities of gold and silver, or contains undue quantities of deleterious elements.

If the metallic copper produced by the operations previously described under I. and II. comes under the description (a) above, it can be refined by furnace treatment only; if it comes under (b) it must be refined electrolytically in order to recover the gold and silver or to obtain it free from the impurities.

Under (a), the furnace employed is of the reverberatory type, and the removal of the impurities is effected by slowly melting the pigs of copper under highly oxidising conditions, and maintaining the bath of molten copper under this condition until the impurities are oxidised and removed, either by volatilisation or by passing as oxides into the copper silicate slag formed. The oxidation of the impurities is facilitated by the fact that metallic copper has the property of dissolving a small proportion of cuprous oxide, which compound is brought into contact with the elements to be oxidised under the very favourable condition of fluidity.

· The oxidising condition of the bath of molten copper is maintained until the impurities are removed, as far as practicable, and the copper contains a maximum quantity of dissolved cuprous oxide. In this condition the metal is said to be 'dry.' After removal of the slag, the next stage consists in reducing the greater portion of the dissolved cuprous oxide, which is effected by depressing poles of green wood below the surface of the bath of metal, when considerable agitation takes place and the cuprous oxide is subjected to the reducing action of the gases given off by the pole.

The process is continued until only a small quantity of cuprous oxide remains, and the copper attains the physical condition known as 'tough pitch,' when it is ladled out into moulds of any required shape.

Under (b), the copper is refined electrolytically. This process depends for its operation upon the fact that if an electric current is caused to pass through a solution of copper sulphate, the copper in the solution is deposited at the cathode, while the acid is set free at the anode. If the anode is composed of metallic copper, then the acid set free on its surface immediately dissolves an equivalent portion of copper which passes into solution, and is, in turn, deposited at the cathode, and the process thus becomes continuous so long as the current passes and there is copper at the anode to be dissolved. Assuming that the solution of copper sulphate is properly made up and maintained, and the voltage and current are suitably adjusted, then only copper will be deposited at the cathode, while the gold and silver and all the impurities contained in the copper anodes will either remain as insoluble slime, collected at the bottom of the vessel in which the operation is conducted, or will pass into the electrolyte. Gold, silver, and lead pass entirely into the insoluble slime ; other elements, such as iron and nickel, pass wholly into the solution, and others again are to be found partly in the slime and partly in the electrolyte. The cathode surface is, to start with, a very thin sheet of electro-deposited copper, and when—as the result of the operation—sufficient copper has accumulated upon its surfaces, it is removed from the bath and is ready for melting and casting into any required shape. In practice, a number of anode plates are hung in a lead-lined wooden tank, and are suitably connected to the positive lead. Alternating with these anode plates are hung the cathode sheets, connected in parallel with the negative lead. A large number of tanks are connected in series, and the current is passed through the whole set of tanks. The electrolyte is caused to circulate through the whole series, and, after it has been in use for some time, a certain proportion must be removed regularly for purification. A quantity of anode copper remains undissolved, and when the tank is to be cleaned, this is taken out for remelting into anodes, the solution is run off, and the slime is removed. This latter is washed and dried, any large particles of copper removed by sieving, and the fine slime is then treated for the recovery of any silver or gold which it may contain.

Copper flue dust. A considerable amount of copper may be carried forward in the waste gases from the furnaces and precautions are now taken to recover it. In modern well arranged plants, capacious flues and dust chambers are provided between the furnaces and the chimney for the deposition of the fine particles of ore carried forward, and for the condensation of copper fume, which is frequently arsenical. The Cottrell process of electrostatic precipitation of dust is sometimes used. The dust obtained is collected from time to time and retreated in reverberatory furnaces or is briquetted and smelted in blast furnaces.

Wet methods. Until recently these had a very limited application in the extraction of copper, but within the last few years have made remarkable strides, and extensive plants are now in operation in which new methods or modifications of the older methods are being used. The wet extraction of copper consists of leaching the ore either in its natural condition or after roasting and in a suitable state of subdivision, with a suitable solvent, in vats fitted with false bottoms and precipitating the copper from the solution thus obtained by suitable means.

Wet methods are specially suitable for the treatment of low grade oxidised ore and for oxidised tailings, but have also been successfully applied to the treatment of material containing the copper as sulphide. The most widely used method consists in leaching the ore with dilute sulphuric acid and recovering the copper from the solution by electrolysis or by precipitation on metallic iron. This method can be applied directly to oxidised ores, but in the case of sulphide ores a preliminary roast, in order to render the copper soluble in the acid, is frequently necessary.

At Rio Tinto the massive cupriferous pyrites is treated without roasting, large heaps of the mineral being allowed to oxidise slowly under the action of air and moisture, and the copper sulphate thus formed is washed out and precipitated on metallic iron. In some cases in which sulphuric acid leaching is followed by electrolytic deposition of the copper, the regeneration of sulphuric acid in the precipitation plant yields a solvent suitable for further leaching operations.

Another method used consists in roasting the cupriferous sulphide material with salt. Soluble copper salts are thus formed which may be recovered by solution and precipitation of the

copper on iron. A modification of this process is also used whereby silver is recovered with the copper.

Other processes are sometimes used in which sulphurous acid, ferric sulphate, ferrous chloride and ammonia are used as solvents.   C. O. B.

COMPOUNDS OF COPPER.

Oxides. Five oxides of copper are said to be known: the quadrantoxide Cu_4O, the trientoxide Cu_3O, the sub- or hemi-oxide Cu_2O, the monoxide CuO, and the peroxide CuO_2. Other oxides have been described, but their existence is not proved.

Copper quadrantoxide is stated to be formed by adding a solution of copper sulphate to a cooled dilute solution of stannous chloride in caustic potash (Rose, Pogg. Ann. 1861, 120, 1). It is an olive-green powder, which rapidly absorbs oxygen from the air. According to Moser (Zeitsch. anorg. Chem. 1909, 64, 200), this product is really a mixture of cuprous oxide and copper.

Copper trientoxide is obtained as a hard yellowish mass by heating cupric oxide at $1500°–2000°$. It is unaffected by any acid except hydrofluoric (Bailey and Hopkins, Chem Soc. Trans. 1896, 269).

Copper suboxide, or hemioxide, red oxide of copper, cuprous oxide Cu_2O, occurs native as *cuprite* or red copper ore, and as *chalcotrichite*.

It may be prepared (1) by heating finely divided copper in air below a red heat; (2) by gently heating a mixture of 5 parts cuprous chloride and 3 parts sodium carbonate in a covered crucible, and separating the oxide by lixiviation; (3) by reduction of an alkaline solution of a copper salt by sugar or certain other organic bodies, as in Barreswil's (Fehling's) solution; (4) by heating in a covered crucible a mixture of 5 parts copper monoxide and 4 parts copper filings; (5) by the electrolysis of copper sulphate solutions under certain conditions (Miller, J. Phys. Chem. 1909, 256; Gillett, *ibid.* 1909, 332); (6) by heating cupric oxide in sulphur dioxide and treating the product with water, when cupric sulphate is dissolved and the cuprous oxide remains: $3CuO + SO_2 = Cu_2O + CuSO_4$ (Hammick, Chem. Soc. Trans. 1917, 111, 384).

This oxide is decomposed by most acids into a cupric salt and copper; hydrochloric acid, however, converts it into cuprous chloride

Cuprous oxide fuses at a bright-red heat. It dissolves in metallic copper and renders it brittle or 'dry' when present in quantity. As much as 4·6 p.c. has been found by Abel in very dry copper, and, according to Watson (J Soc. Chem. Ind. 1883, 154), from 1 to $2\frac{1}{2}$ p.c. is present in ordinarily good copper

It is largely used in the manufacture of *ruby glass*, and for the production of a red glaze on pottery (Louth and Dutailly, Mon. Ceram. et Verr. 19, 237), and, together with the black oxide, forms one of the so-called *copper paints* used for painting ships' bottoms.

A yellow form of the oxide is produced by the action of alkali on cuprous chloride, or better by the reduction of a cupric salt by means of hydroxylamine in presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure

copper. It may also be obtained by the reduction of Barreswil's (Fehling's) solution in presence of a deficit of tartrate. The yellow precipitate thus formed is not a definite hydrate, but is a colloidal form of the oxide with an indefinite amount of water (Gröger, Chem. Zeit. Rep. 1902, 197). It quickly changes to an orange or brick-red colour and can then be dried unchanged. The dried product contains from 2–3 p.c. of adsorbed water. At a low red heat it loses this water and changes into the red crystalline form. The yellow cuprous oxide is to be regarded as a primary metastable form, the red crystalline form being the stable one. It is a powerful reducing agent, especially in ammoniacal solution. This solution, which is colourless, immediately becomes blue from the formation of the monoxide on exposure to the atmosphere, and thus forms a delicate test for oxygen. The hydrated oxide dissolves in a concentrated solution of magnesium chloride.

This oxide is produced in Hoepfner's process for extracting copper from ores, &c., with cupric chloride solution. Cuprous chloride is formed and treated with alkali to obtain cuprous oxide (J. Soc. Chem. Ind. 1893, 932; Eng. Pat. 18900, 1892).

Copper monoxide, cupric oxide, black oxide of copper, 'copper oxide' CuO, occurs as *melaconite* or *black copper*, especially at Lake Superior.

It may be prepared by heating the nitrate or carbonate to dull redness or the sulphate to intense redness. The decomposition of the sulphate is the basis of Adcock's process for the preparation of the oxide direct from the natural carbonate or sulphate (Eng Pat. 11678, 1900). The copper oxide used for organic analysis, &c., may be prepared by moistening copper scale (the mixture of suboxide and black oxide obtained while working copper sheet, &c.) with nitric acid, and igniting.

An electrolytic method of preparing the oxide has been described by Miller (J. physikal. Chem. 1909, 256); and by Luckow (Zeitsch. Elektrochem. 1897, 482).

Copper oxide is a black powder which agglomerates when heated, and fuses at the melting-point of copper, forming cuprous oxide, or Cu_3O, according to the temperature. It can be made to crystallise in regular tetrahedra. It is slightly hygroscopic, especially when in powder. When heated with organic substances or certain gases, it is reduced to metal. The metal produced by reduction in hydrogen always contains that gas, but if the oxide be reduced in formic acid vapour, the metal is quite free from hydrogen and is suitable for organic analysis (Weyl, Ber. 15, 1138).

It dissolves in acids with formation of cupric salts. In oils, &c., it is soluble to some extent; it is for this reason that copper cooking vessels require such constant cleansing.

. Copper oxide is used in ultimate organic analysis; to make green and blue glass and glazes, and to some extent as a pigment. It has also been used as one electrode of a galvanic cell (v. Lelande and Chaperon, Bull. Soc. chim. [2] 49, 173).

Cupric hydroxide $CuO·H_2O$ may be prepared by precipitating a solution of a copper salt by addition of alkali and washing rapidly.

When heated with water, it becomes black and amorphous.

A colloidal form of the oxide has been obtained by Paal and Leuze (Ber. 1906, 1545), which gives blue-violet solutions, and when dry retains its solubility indefinitely.

The hydroxide is used as a blue pigment by paper stainers, but becomes green on exposure. It corresponds closely with certain of the highly basic carbonates sold as *verditers.* According to Dumas, it is best prepared as follows : 6 parts of copper sulphate are dissolved in water and mixed with a solution of 3 parts of calcium chloride. The clear liquid is decanted from the precipitated calcium sulphate and is mixed with 1½ parts of lime made into a cream with water. The greenish precipitate is collected, washed, and mixed with one-fourth its weight of slaked lime and as much pearl ash, and to render the colour more permanent, one-fourth its weight of ammonium chloride and one-half its weight of copper sulphate are usually added.

The hydrated oxide dissolves in ammonia, the saturated solution in strong ammonia being known as 'Schweitzer's reagent,' or *cuprammonium.* This solution has the property of gradually dissolving *cellulose* with formation of a viscid solution which is used for the preparation of the 'Willesden papers,' and for the production of 'artificial silk' on the large scale. This process consists in injecting the copper-cellulose solution into strong solutions of alkali or acid. In either case, coagulation takes place with formation of a fibre of cellulose corresponding in thickness to the diameter of the jet.

An aqueous solution of sodium hydroxide of sp.gr. 1·345 1·370, or of potassium hydroxide of sp.gr. 1·453–1 498, will dissolve 0 78 grm. of cupric hydroxide in 100 c.c giving a bright blue solution which yields no precipitate when boiled. If a more dilute alkali solution be used the solution is not stable when further diluted and subsequently boiled (Justen-Mueller, Compt. rend. 1918, 167, 779).

Cuprammonium solutions are prepared on the large scale by the joint action of oxygen and ammonia on metallic copper at temperatures near 0° (Schaefer, U S. Pat. 884298, 1908 ; Bronnert, Frémery, and Urban, Eng. Pat. 1763, 1900 ; Lecœur, Fr. Pat 374277, 1906).

Bellot has patented a continuous process of manufacture, using a series of closed vessels (Fr. Pat. 335207, 1903).

The solution should be purified by dialysis, as the presence of crystalline salt favours its decomposition (Lecœur, Fr. Pat. 362986, 1906). Addition of 1–2 p.c. of polyhydric alcohols, carbohydrates, gum, &c., to cuprammonium solutions increases their stability and prevents the deposition of cupric hydroxide (Friedrich, Eng. Pat. 4104, 1909), and the presence of such substances facilitates manufacture of the solution, making it possible to employ copper concentrations up to 5 p.c. without cooling (Fr. Pat. 399911, 1909).

Chattaway has shown (Proc. Roy. Soc. 1908, 80, A, 88) that by the reduction of a cuprammonium solution with aromatic hydrazines, copper mirrors can be deposited on glass.

Dawson states that a solution of cupric hydroxide in ammonia contains copper as the base $Cu(NH_3)_4 (OH)_2$ (Zeitsch. physikal. Chem. 69, 110). (For a general discussion of the constitution of cuprammonium salts, *see* Horn and Taylor (Amer. Chem. J. 1904, 253), and Horn (*ibid.* 1907, 475).)

Copper dioxide, copper peroxide CuO_2, is obtained by the action of hydrogen peroxide on cupric hydroxide in neutral solution at 0° (Kruss, Ber. 1884, 17, 2593 ; Moser, Zeitsch. anorg. Chem. 1907, 54, 121). The crystalline precipitate is washed with water, alcohol, and ether at 0°, and dried *in vacuô*. It has a yellowish-brown colour, and decomposes at 180°, forming cupric oxide.

SALTS. Two series of copper salts are known, *cuprous* and *cupric.* The former are mostly insoluble in water, and are of but little commercial importance. They act as powerful reducing agents and readily pass into the cupric condition. Cupric salts are mostly soluble, and are of wide application.

Cuprous chloride Cu_2Cl_2 may be prepared, amongst other methods, by boiling cupric chloride with hydrochloric acid and copper turnings. On addition of water it is precipitated in white crystals.

Zulcoga has suggested (Rev. Chim. Ind. 1900, 107) that the cuprous chloride solution used in the extraction of silver from its ores should be prepared by mixing solutions of cupric sulphate and of cupric sulphate and sodium chloride.

Cuprous chloride melts below a red heat into a yellow transparent mass. The dry crystals become yellowish on exposure to light ; if moist, they acquire a dirty-violet tinge. Plates of copper coated with this chloride by the action of chlorine will take photographic impressions, but cannot be made to withstand exposure to light (e Carlemann, J. pr. Chem. 63, 475 ; and Priwoznik, Dingl poly. J. 221, 38).

Cuprous chloride combines with ammonia to form three compounds

$Cu_2Cl_2 \cdot NH_3$, $Cu_2Cl_2 \cdot 3NH_3$, $Cu_2Cl_2 \cdot 6NH_3$
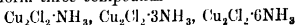
Cuprous bromide and iodide form compounds analogous to the last two (Lloyd, J. Phys. Chem. 1908, 398).

The hydrochloric acid solution, when exposed to air, absorbs oxygen and acquires a brown colour, subsequently depositing a pale bluish-green insoluble copper oxychloride

$$CuCl_2 \cdot 3CuO, 4H_2O$$
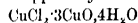
An identical substance used as a pigment, and known as *Brunswick green*, is prepared by boiling a solution of copper sulphate with a small quantity of bleaching powder solution ; or by moistening copper turnings with free exposure to air. It occurs in nature as *atacamite.*

The use of the oxychloride in preference to the sulphate for destroying mould on vines, &c., is recommended. 200–250 grams per litre of water are employed (Deletrez, J. Soc. Chem. Ind. 1909, 438).

When a solution of cuprous chloride in potassium chloride, acidified with hydrochloric acid, is treated with acetylene, a yellow precipitate of $Cu_2Cl_2 \cdot C_2H_2$ is formed. Other compounds containing copper oxide or potassium chloride can be obtained by varying the conditions (Chavastelon, Compt. rend. 132, 1489).

Acetylene reacts with solutions of cuprous

chloride in ammonia to form a blood-red precipitate of *cuprous acetylide*, which, on dehydration, has the formula Cu_2C_2, and is highly explosive . (Scheiber, Ber. 1908, 3816). Its decomposition by acids has been used as a means of preparing pure acetylene. A colloidal solution of copper acetylide has been prepared by Küspert (Zeitsch. anorg. Chem. 34, 453) (*v.* ACETYLENE).

Cuprous bromide Cu_2Br_2 is obtained by the union of its elements or by boiling a solution of cupric bromide with copper, and forms a brown crystalline mass.

Cuprous iodide is the only known iodide of copper, and is obtained as a white precipitate by adding potassium iodide to a solution of copper sulphate containing ferrous sulphate or sulphurous acid. It has a sp gr. 5 653 at 15° (Spring, Rec. trav. chim. 1901, 79), melts without decomposition at 628°, and is practically insoluble in water.

Cuprous sulphite Cu_2SO_3,H_2O is obtained in microscopic nacreous plates by passing sulphur dioxide into a hot solution of cuprous acetate in acetic acid. It forms double salts with the alkali sulphites. *Cupro-cupric sulphate* $Cu_2SO_4 \cdot Cu_2SO_3,2H_2O$ is a red microcrystalline powder.

Cuprous sulphate Cu_2SO_4 can be prepared by the action of dry dimethyl sulphate on dry powdered cuprous oxide (Recoura, Compt. rend. 148, 1909, 1105). A compound of cuprous sulphate and carbon monoxide $Cu_2SO_4 \cdot 2CO,H_2O$ has been obtained by Joannis (*ibid.* 1903, 615), by reducing cuprammonium sulphate with hydroxylamine. Péchard has made ammonio-cuprous sulphate $Cu_2SO_4 \cdot 4NH_3$ (*ibid.* 1903, 504).

Cuprous sulphide Cu_2S occurs as *chalcocite* or *copper glance*. It may be prepared by heating copper to redness in sulphur vapour, or by heating a mixture of copper and sulphur It melts at $1130° \cdot D_4^{25°}$ 5 785. It is dimorphous, and has an inversion temperature at 91°.

Cupric chloride $CuCl_2$ may be prepared as a fused, liver-coloured, anhydrous mass by heating copper in excess of chlorine. In solution it may be prepared by dissolving the oxide in hydrochloric acid. It crystallises in grass-green prisms or needles containing 2 molecules of water. They become pale-blue when dried *in vacuó.* The anhydrous salt is obtained on gradual addition of a large excess of conc. sulphuric acid to a solution of the chloride (Viard, Compt. rend. 1902, 135, 168).

° Cupric chloride is very deliquescent, and is soluble in alcohol. When a small quantity of potash is added to the aqueous solution, a pale-blue basic oxychloride $2CuO \cdot CuCl_2, 4H_2O$ is precipitated. It turns to a black anhydrous powder when heated, but again becomes green with absorption of 3 molecules of water when moistened. It is an intermediate product in the manufacture of *verditer* (*v.* Copper carbonates).

Cupric chloride is used in calico printing, in the manufacture of *methyl violet*, and for the oxidation of *Cutch colours.*

Green has shown that the chloride is a very effective disinfectant (Zeitsch. fur Hygiene), 1893, 495).

When cupric chloride solution is mixed with excess of potassium thiocyanate solution, *cupric thiocyanate* $Cu(CNS)_2$ is produced. This is

slowly acted on by water and is ultimately reduced to *cuprous thiocyanate* CuCNS with formation of carbon dioxide, ammonia, carbamide, hydrogen cyanide, thiocyanic and sulphuric acids (Philip and Bramley, Chem. Soc. Trans. 1916, 109, 597).

Cupric bromide $CuBr_2$ is obtained by dissolving cupric oxide in hydrobromic acid and evaporating *in vacuó.* It is dark-coloured, very deliquescent, and, when heated, decomposes into cuprous bromide and bromine. It is used as an intensifier in photography, and for that purpose is made by dissolving in water a mixture of anhydrous copper sulphate and potassium bromide (Akt. Ges. f. Anilinfabr. D R. P. 201168, 1907).

Cupric sulphate, *Blue vitriol* $CuSO_4, 5H_2O$, occurs naturally at Copaquire, Chile, the rock containing over 12 p c of the hydrated salt (Walker, Eng. and Min. J. 1903, 710). This salt may be prepared by dissolving copper or its oxide in sulphuric acid.

It is prepared on the large scale from metallic copper in the following way : Old copper plates from the sheathing of ships, &c , are heated to strong redness in a reverberatory furnace, and an excess of sulphur is thrown in and the doors are closed. When combination is complete, the doors are reopened and the heat is raised to dull redness to oxidise the sulphide into sulphate. The mass, while hot, is thrown into dilute sulphuric acid, allowed to settle, the solution decanted, concentrated, and crystallised. The sulphate so produced is of considerable purity. *Coarse copper* and *copper glance* or other sulphurous copper ores are similarly treated. Pauffin and Couvert have patented a process for the direct manufacture of the sulphate from the metal (Fr. Pat. 399413, 1909). (*See* also Walker, U.S. Pat. 788862, 1905).

.When much iron is present, as in most copper ores and especially in copper pyrites, it would be impossible to separate the copper and ferrous sulphates by crystallisation, because, although copper sulphate crystallises normally with 5 molecules of water, it forms, in presence of ferrous sulphate, crystals isomorphous with that salt and containing 7 molecules of water. By carefully adjusting the temperature at which the sulphide is roasted, however, the iron salt may be converted into the oxide while the copper sulphate remains almost unaffected. The iron may be removed by heating the solution of the sulphates to 180° in a copper boiler under pressure. Ferrous sulphate crystallises out and is filtered off (Gin, Fr. Pat. 328800, 1903). The iron may be oxidised and thus separated from the copper by boiling the solution with a little nitric acid. It may also be precipitated as oxide by boiling with copper oxide, or by boiling with lead peroxide with subsequent addition of a little barium carbonate.

Crude copper or the ore may be roasted in air, and then treated with sulphur dioxide to form the sulphate (Gin, Zeitsch. angew. Chem. 1903, 566 ; Eng. Pat. 5230, 1903).

Darier has patented a process in which cupric chloride is formed by the action of chlorine and water on the metal, and is then decomposed by sulphuric acid, with formation of the sulphate and regeneration of hydrochloric acid (Fr. Pat. 350421, 1904).

When the sulphate is required for purposes

where the presence of iron is not injurious, such liquors, or the mother liquors from which the purer salt has been separated, may be at once crystallised out, with the formation of crystals containing both iron and copper. Much of the 'agricultural copper sulphate' is of this class. The 'Salzburg vitriol,' prepared at Buxweiler, also contains both iron and copper. According to Lefort (Compt. rend. 26, 185), it consists of $CuSO_4\cdot3FeSO_4,28H_2O$. 'Cyprian vitriol,' prepared at Chessy from zinciferous copper ores, forms blue rhombic prisms, which contain according to Lefort, $CuSO_4\cdot3ZnSO_4,28H_2O$.

The copper may be separated from the ferrous mother liquors by placing them in vats containing iron plates upon which the copper is slowly deposited.

Apparatus for the solution of copper oxide in sulphuric acid upon a large scale has been described by Coste (Fr. Pat. 392617, 1908). If copper be known to contain silver or gold, as is the case with that from the Harz, it is treated with sulphuric acid diluted with its own volume of water, the copper being thus dissolved while the silver and gold are unattacked.

Argentiferous copper ores are roasted in a reverberatory furnace, and added in small charges to sulphuric acid and digested until the solution contains but little free acid. The solution is then decanted from the precipitated lead and gold, and is concentrated and run into lead-lined tanks containing plates of copper, upon which all the silver and part of the antimony and arsenic are deposited, while the greater proportion of the bismuth is precipitated as a basic sulphate, and the iron is reduced to the ferrous condition. The liquor is then crystallised, the mother liquors being used for treating a fresh quantity of ore. Copper sulphate is obtained of great purity and in considerable quantity in the refining of silver by precipitating it upon plates of copper from its solution as sulphate (v. SILVER).

An electrolytic process for the production of the sulphate consists in using a solution of sodium sulphate and copper electrodes, a current of carbon dioxide being passed through the liquid. Copper is dissolved from the anode as sulphate, while sodium carbonate is produced at the cathode. These react, regenerating sodium sulphate and precipitating copper carbonate, which is collected and dissolved in sulphuric acid (Kroupa, J. Soc. Chem. Ind. 1906, 78).

Palas and Cotta have also described electrolytic processes for the production of the salt (Eng. Pat. 9806, 1899, and 17485, 1900).

The electrolytic production of the sulphate from 'cement copper waters' has been described by Rambaldini (Chem. Zentr. 1909, i. 1675).

It is stated that copper sulphate is sometimes adulterated with ferrous sulphate and Prussian blue to the extent of 90 p.c. (J. Soc. Chem. Ind. 1900, 84).

Copper sulphate crystallises in large transparent blue, doubly oblique rhombic prisms of sp.gr. 2·28, of the formula $CuSO_4,5H_2O$. According to Poggiale, their solubility in 100 parts of water is :

10°C.	20°	30°	40°	50°
36·59	42·31	48·81	56·9	65·83
70°	80°	90°	100°	
94·60	118·0	156·44	203·32	

When heated, it loses 2 molecules of water at 30°, 2 more at 93°-98°, and at 232° becomes anhydrous, white, and hygroscopic, and combines with water with considerable evolution of heat. At 341° the anhydrous salt begins to decompose (Wanjukow, Chem. Zentr. 1909, ii. 1124). The sp.gr. of the anhydrous salt is 3·606 (Thorpe and Watts). It combines with water in alcohol and other organic liquids with production of a blue colour, and may be used for ascertaining the presence of water in those substances, but the test is not delicate. The anhydrous salt is also soluble in anhydrous methyl alcohol, and produces a bluish-green solution (Klepl, J. pr. Chem. 1882, 25, 526).

Copper sulphate absorbs hydrogen chloride with evolution of heat, forming cupric chloride and liberating sulphuric acid. It is therefore used to remove hydrogen chloride from such gases as chlorine or carbon monoxide. A similar reaction occurs in solution.

When mixed in solution with molecular proportions of potassium and other sulphates, it produces well-defined, crystalline double sulphates. Several basic sulphates are known.

The sulphate is the most important of the copper salts. It is largely used in calico printing, principally in connection with potassium dichromate or iron mordants ; in black dyeing with logwood ; directly or indirectly for the preparation of most pigments containing copper ; and to prevent rot in timber. In agriculture the crude sulphate containing ferrous sulphate is used to a considerable extent to prevent smut in seeds. The seeds are soaked for some hours in a weak solution of the sulphate, and are sown within 24 hours.

A 10-20 p.c. solution of copper sulphate, preferably mixed with lime, is applied to vines with great benefit. A small quantity is found in the vines and must, but the tannin and sulphur introduced before fermentation appear to remove it in most cases.

Karsten has stated (v. J. Soc. Chem. Ind. 1896, 367) that attacks of illness resembling dysentery have been caused by a wine which contained copper in such quantity as to form a visible deposit on steel in 12 hours. Its presence was due to spraying the vines with a copper salt.

An effective wash for vines is prepared by boiling 25 parts of sodium carbonate and 25 parts of resin in 100 parts of water, and then diluting and adding copper sulphate (J. Soc. Chem. Ind. 1899, 155).

Copper sulphate is used in preparing copper ferrocyanide, a solution of which, in potassium citrate solution, is used as a toning-bath for photographs (Ferguson's Copper Toning, ibid. 1900, 465).

Copper sulphate is also used in dyeing to make diazo- colours permanent to light. The dyed fabric may be treated with the salt (Graebling, ibid. 1905, 797), or it may be added to the diazotising bath (Grossmann, Färber-Zeit. 9, 328).

Cupro-tetrammonium thiosulphate CuS_2O_3 $(NH_3)_4$, has been proposed as an ingredient of detonator compositions, which although less sensitive are alleged to possess advantages over mercury fulminate compositions, as being cheaper, less unhealthy, simpler, and less dangerous to manufacture. The thiosulphate is

made by adding excess of strong ammonia solution to a hot saturated solution of copper sulphate, and thereafter adding an equivalent amount of sodium thiosulphate, dissolved in hot water. The salt separates out as the solution cools; it is washed with a weak solution of ammonia, and dried at a temperature not exceeding 50°. The violet-blue crystals are slightly soluble in water, not hygroscopic, insensitive to light, and very stable. Compositions suitable for various purposes are made by mixing with potassium chlorate, powdered glass, antimony trisulphide and lead thiosulphate (Herz, Zeitsch. ges. Schiess. u. Sprengstoffw. 1912, 7, 284; J. Soc. Chem. Ind. 1912, 31, 903)

Potassium copper nitrite $K_2Cu(NO_2)_4$ is obtained by mixing cold saturated solutions of copper sulphate and potassium nitrite, adding methyl alcohol, filtering, and adding ethyl acetate to the clear, green filtrate when long crystals of the salt separate. *Rubidium copper nitrite* of similar composition may be obtained in like manner (Kurtenacker, Zeitsch. anorg. Chem. 1913, 82, 204). *Basic copper nitrites* $3Cu(OH)_2 \cdot Cu(NO_2)_2$ and $2Cu(OH)_2 \cdot Cu(NO_2)_2$ are also known.

Cupric nitrate $Cu(NO_3)_2$ may be prepared by dissolving copper or the oxide or carbonate in nitric acid. The solution at temperatures above 20° deposits dark-blue crystals containing 3 molecules of water, which melt at 114·5° and boil at 170° with evolution of nitric acid and formation of a green basic salt. This basic salt may also be prepared by boiling the solution of the nitrate with copper or copper hydrate, or with a little alkali (v. also *Copper carbonates* for an application of the basic nitrate).

The anhydrous salt may be obtained by the action of nitric anhydride on the hydrated salt. It is a white, deliquescent powder, decomposing at 155°–160° (Guntz and Martin, Bull. Soc. chim. 1909, 5, 1004).

Copper nitrate is used to a slight extent in dyeing and calico printing, and a solution, prepared by mixing solutions of copper sulphate and calcium nitrate, is used in viticulture (Gouthière et Cie and P. Ducancel, Fr Pat. 395806, 1908)

Cupric sulphide CuS occurs as *covelite* or indigo copper in blue flexible plates, in Vesuvian lava, in Chile, and in the copper-mines of Mansfeld. It may be prepared by heating cuprous sulphide with sulphur at a temperature not above the boiling-point of sulphur; by digesting cuprous sulphide with cold strong nitric acid; or by precipitating a copper solution with sulphuretted hydrogen $\cdot D_4^{25}$ 4·68. On the large scale it is obtained as a paste by precipitating a solution of the sulphate with sodium sulphide. This paste is used in calico printing for the development of aniline black.

The preparation and use of copper sulphide for thermo-couples has been described (Eng. Pat. 11300, 1905).

Rieder has used (Zeitsch. Elektrochem. 1902, 370) an electrolytic method for the preparation of this compound.

A brownish-red *persulphide of copper* has been obtained by Bodroux by adding a solution of calcium pentasulphide to a solution of copper acetate at 0° (Compt. rend. 130, 1397).

Copper acetate v. *Metallic acetates*, art. ACETIC ACID.

Copper arsenite v. *Scheele's green*, art. ARSENIC.

Cupric phosphate is of no technical interest. A brilliant green colour containing a basic phosphate, prepared by heating a mixture of copper acetate, sodium phosphate, and ammonia, has, however, been used in calico printing (Bourcart, Mon. Sci. [3] 4).

Phosphorus combines in several proportions with copper, and produces true alloys, which in many cases are of great value.

Heyn and Bauer state that the phosphorus exists in the alloy as Cu_3P and Cu_5P_2 (J. Soc. Chem. Ind. 1906, 1047) The latter compound has been obtained by Rubénovitch by the action of phosphine on copper sulphate (Compt. rend. 127, 270).

Copper silicide (*Cuprosilicon*) Cu_4Si is obtained when copper and silicon are heated together in the electric furnace (Vigouroux, Compt. rend 1896, 122, 318; Lebeau, *ibid.* 1906, 142, 154) It is now manufactured in Germany and America by this process (Stemhart, Eng. and Min. J. 1899, 67, 710), and is used for purifying and hardening copper, and for adding to tin-, zinc-, and aluminium-bronzes to increase their tensile strength and hardness

Cuprosilicon can be prepared pure by heating together 17 parts silicon and 9 parts copper, in hydrogen, and removing the excess of silicon by solution of sodium carbonate. It is silver-white, with a metallic lustre, and is hard and brittle The sp.gr is 7 58, and it is attacked by chlorine and *aqua regia* (Vigouroux, Compt. rend. 1906, 142, 87; *see also* Philips, Métallurgie, 1907, 4, 587; and Lebeau, *ibid.* 141, 828).

Copper carbonates. The normal salt has not been prepared, but several basic carbonates are known, and used as blue and green pigments. Basic copper carbonate occurs native as *malachite* $Cu(HO)_2 \cdot CuCO_3$, and as *azurite* or *chessylite* $Cu(HO)_2 \cdot 2CuCO_3$. When ground, these minerals form a fine but expensive pigment.

An anhydrous basic carbonate is precipitated on addition of a solution of sodium carbonate to a hot solution of copper sulphate or nitrate. (For a complete description of all the known basic carbonates of copper, *see* Pickering, Chem. Soc. Proc. 1909, 188. *Cf.* Dunnichff and Lal, Chem. Soc. Trans. 1918, 113, 718.) Commercial basic carbonates of copper differ considerably in composition: the amount of carbon dioxide present is below that required for malachite or azurite. A definite basic salt is known of the composition $2CuCO_3 \cdot 5Cu(OH)_2$.

Under the names *Verditer green*, *Verditer blue*, *Bremen green*, and *Bremen blue*, this salt is largely prepared for paper staining, &c. According to Habich (Technologiste, 17, 413), the following processes are in use. A hundred parts of old copper sheathing from which impurities, oxide, &c., have been removed by digestion in dilute sulphuric acid, is cut into pieces and mixed with a paste formed by moistening a mixture of 99 parts potassium sulphate and 100 parts common salt, and the mixture is stirred occasionally for some months to ensure thorough exposure to the atmosphere. The action appears to consist in the production of cupric chloride,

which, in presence of the metal, becomes converted into a basic chloride, and finally, by the action of the oxygen, into an oxychloride. If the oxidation be incomplete, the subchloride is not completely oxidised, and, as it, when subsequently decomposed by alkali, gives an orange-red precipitate of suboxide, the pigment would be lowered in value. The oxychloride may also be similarly prepared from a mixture of 100 parts copper, 60 parts common salt, and 30 parts strong sulphuric acid diluted with three times its volume of water ; or by treatment, with free atmospheric exposure, of copper with a solution of cupric chloride in hydrochloric acid.

To 100 kilos. of this thick magma of oxychloride, which has been washed by decantation, a concentrated solution containing 7 kilos. copper sulphate and 40 kilos. concentrated soda solution (32°–36°Bé.) is added. The mixture is vigorously stirred and poured at once into 150 kilos. of soda solution (20°Bé.). The precipitate is washed, passed through a fine hair sieve, and dried spontaneously or at a temperature below 25°. If hot air be used in the drying, it must be quite free from acid or sulphur gases. To produce the finest colour, desiccation must be perfect.

Habich recommends the following process for making a *verditer* which has a very different composition from the above. A solution of copper oxide in nitric acid is treated with potassium carbonate, which is added in portions until most, but not all, the copper has been precipitated. The green precipitate is washed and introduced into a solution of copper nitrate whereby it is converted into a heavy green insoluble basic nitrate. This is digested in a solution of potassium zincate (formed by dissolving zinc in caustic potash solution). A dark-blue pigment, of great ' body ' but little weight, is thus produced. It contains zinc and copper, apparently combined as a double oxide or as ' copper zincate,' and a small quantity of basic copper nitrate.

Verditer may be prepared by agitating a solution of copper nitrate with chalk. The washed pasty precipitate is mixed with 8–10 p.c. of freshly burnt lime with production of a fine velvety blue pigment. The precipitate without addition of lime is green.

According to Gentele, the following process is adopted at Bremen, Cassel, &c. ; 225 lbs. sea salt and 222 lbs. blue vitriol, both free from iron, are mixed dry and ground between millstones with water to a thick paste. This paste is mixed in strata with 225 lbs. of clean copperplate cut into pieces about 1 inch square, in wooden chests made without nails, and the mixture is allowed for about 3 months with the maximum exposure to air, the whole being well mixed and exposed about once a week. When the action is complete, the undissolved metal is removed and the precipitate is washed with a minimum of water, filtered and thrown into a tub. To 180 lbs. of the magma 12 lbs. of hydrochloric acid (13°Bé.) is added, and the mixture is stirred and left for 24 or 36 hours. Six volumes of this solution is mixed with 15 volumes of caustic alkali (19°Bé.) followed after an interval by 6 volumes of water. The mass is well mixed and left for 36–48 hours, and is then well washed by decantation, filtered,

exposed for some time in a moist condition to the air, and finally dried (*v. also Copper monoxide*).

COPPER-GLANCE or **Chalcocite.** Native cuprous sulphide Cu_2S, crystallising in the orthorhombic system. Excellent twinned crystals were formerly found in abundance in the neighbourhood of Redruth in Cornwall (hence the name redruthite) and Bristol in Connecticut ; usually, however, the mineral is found as compact masses. It is iron-black with metallic lustre, but, on exposure to light, it soon becomes dull with a powdery black coating. It is soft (H. 2½) and sectile, and can be readily cut with a knife ; sp.gr. 5·7. It occurs in veins of copper ore, and is often of importance as an ore, especially when it contains small amounts of silver. Isomorphous with copper-glance is the mineral *stromeyerite* $(Ag,Cu)_2S$, which has been found in considerable quantities in the Altai Mountains in Siberia. L. J. S.

COPPER PAINT *v.* COPPER.

COPPER PYRITES or **Chalcopyrite.** A sulphide of copper and iron $CuFeS_2$, containing when pure 34·5 p c. of copper, and the most important of the ores of copper. It has a characteristic brassy-yellow colour with metallic lustre, and on the surfaces often displays a brilliant iridescent tarnish (peacock-copper-ore). It often occurs together with, and intimately intermixed with, iron pyrites, from which it can be distinguished by its deeper colour and lower degree of hardness ; copper pyrites (H. 3½–4) is readily scratched with a knife, giving a greenish-black powder, whilst iron pyrites (H. 6–6½) is scratched only with difficulty or not at all. It occurs in mineral-veins and in bedded deposits, and by its alteration gives rise to many secondary copper minerals. Crystals are tetragonal with inclined hemihedrism, but only rarely are they distinctly developed ; sp gr. 4·2. L. J. S.

COPRA and **COPRA OIL** *v.* COCO-NUT OIL.

COPROLITES. Concretionary mixtures of calcium phosphate and calcium carbonate, derived from the excrements of certain extinct fishes and reptiles. Formerly much used in the manufacture of superphosphate of lime (*v.* FERTILIZERS).

COPROSMA. The bark, and more especially the roots, of the *C. grandiflora, C. linariifolia,* and *C. areolata,* which belong to the natural family of the *Rubiaceæ,* and are widely distributed in New Zealand, possess tinctorial property (Aston, New Zealand, J. Sci. Tech. 1918, 1, 3), and being related to madder probably contain either alizarin itself or an allied colouring matter. Thus an alcoholic extract of the *C. grandiflora* is coloured purple by alkali, and becomes yellow on addition of acid. From the acid solution, by means of ether, an orange-yellow crystalline substance can be isolated in small amount. A. G. P.

COPYING or **INDELIBLE INK PENCILS.** Unlike iron-gall copying-inks, which will only yield good copies for a relatively short time after writing, solutions of aniline dyestuffs produce writing from which copies may be taken at any subsequent period. In copying-ink pencils the aniline dyestuff, usually methyl violet, is incorporated with graphite, kaolin clay or other basic material. The preparation

of pigments for this purpose was claimed by Petit (Eng. Pat. 4090 of 1874), and their composition was first described by Viedt (Dingl. poly. J. 1875, 216, 96). At the present time these pencils are seldom employed for copying purposes, and their chief use is as a substitute for ink, since they produce a writing which cannot be erased so readily as the marks of a lead pencil. Hence they are frequently described as indelible pencils, although the description is only relatively correct Lehner (Ink Manufacture, 1902, p. 125) gives the composition of four kinds of these pencils made by Faber in Bavaria. The aniline dyestuff ranged from 25·5 to 50 p.c , graphite from 24·5 to 37·5 p.c., and kaolin clay from 12·5 to 50 p.c

Specimens of these pencils examined by Mitchell (Analyst, 1917, 42, 1) had the following composition :—

Origin	Mois-ture	Residue Insol. in water or alcohol	Dyestuff	Loss on ignition (graphite, &c)	Ash (kaolin, &c.)
	p.c	p.c	p c	p c	p.c
American	2·35	76·45	21·20	27·09	47 36
,,	7·48	51·53	40 99	25 48	31·92
,,	2·30	60 89	36·81	56·84	4·05
,,	3 75	63 95	32 30	13·90	50 05
Austrian	3 56	47·14	49·94	44·14	3·00
British	2·72	65·48	31 80	62·08	3 40
,,	4 53	73·05	22 42	69 17	3 88
German	3 72	64·48	31·80	11·86	52·86
,,	6·33	59·83	33 84	7·61	52 22
,,	3 83	57·59	38 58	40·01	17·58

Pigments used in copying-ink pencils may be classified into four main groups –viz. (1) those composed of graphite and dyestuff only ; (2) those in which the dyestuff has been incorporated with approximately equal proportions of kaolin and graphite , (3) those in which the kaolin is largely in excess ; and (4) those in which the graphite predominates. The dyestuff is usually methyl violet, but copying-ink pencils in which red or blue aniline dyes are used are also sold.

The copying properties depend not only on the proportion of the dyestuff, but also on the influence of the basic material. Pencils in which a large proportion of alumina is present yield only faint copies, even when the pigment contains a large amount of the dyestuff. Although methyl violet is usually regarded as a very fugitive dyestuff, experiments have shown that under certain conditions the writing done with these pencils is more permanent than writing done with ordinary ink.

C. A. M.

CORAL is the calcareous substance secreted by many varieties of five kinds of organisms, viz. (1) *Actinozoa*, the principal constituents of coral reefs ; (2) *Hydrozoa*, the large common corals known as millepores ; (3) *Bryozoa*, delicate corals in various forms, resembling mosses, branches, thin filamentary deposits, or more solid masses (in the Palæozoic limestone formations this species of coral abounds) ; (4) *Foraminifera*, chambered shells belonging to

lowly organisms, mostly of very minute size ; (5) *Nullipores*, which, although closely resembling millepores, are veritable algæ or sea-weeds ; they may be readily distinguished from the millepores by the absence of perforations.

Coral is simply a secretion corresponding to the bone of vertebrates or the shell of mollusca, and is composed almost entirely of calcium carbonate derived from sea-water and from the food of the coral-making polyps.

Ordinary coral is somewhat harder than limestone or marble, and, when tapped with the hammer, gives out a ringing sound clearer than is elicited from ordinary calcium carbonate. The sp gr. of 15 specimens examined by Silliman, averaged 2·523

COMPOSITION OF CORAL

S P Sharples (Amer. J. Sci. 31, 168) found

	Calcium carbonate	Calcium phosphate	Water and organic matter
Oculina arbuscula, N Carolina	95 37	0 84	3·79
Manicina areolata, Florida	96 54	0 50	2·96
Agaricia agaricites, Florida	97 73	0·53	1 64
Siderastrœa radians, Florida	97 30	0·28	2·42
Madrepora cervicornis, Florida	98 07	0·32	1 93
Madrepora palmata, Florida	97·19	0·78	2·81

Small and variable quantities of magnesium carbonate, calcium sulphate, calcium fluoride, alkaline chloride, silica, and oxide of iron are found in corals.

The red coral, *Corallium rubrum*, varies in colour from crimson to rose, the latter being the rarest and, therefore, the most prized. It is gathered from the rocky bottom and shores of the Mediterranean ; and it occurs most abundantly at a depth of 25–50 feet ; although, according to Dana, it may be found as deep as 1000 feet. Forchhammer found 2·1 p.c. magnesia in *Corallium rubrum*, and 6·36 in *Isis hippuris*. According to Trommsdorff, the red pigment of coral is a resin soluble in oil of turpentine, and, after removal from the coral by this solvent, is easily soluble in alcohol and ether, but insoluble in caustic potash. In a red madrepore, Vauquelin found a red colouring matter, which was turned violet by alkalis. Moseley has described in some corals and allied organisms a red colouring matter (*Polyporphyrin*) which is insoluble in water, glycerol, alcohol, ether, and in strong solutions of ammonia and potash. It is soluble in moderately strong sulphuric, nitric, or hydrochloric acids. For the formation and distribution of coral and coral-reefs, &c. v. Corals and Coral Islands, J. D. Dana; Coral-Reefs, Darwin ; Murray, in Proc. Roy. Soc. Edinb. 1880, 505. *See also* Forchhammer, J. Pharm. Chim. 49, 52 ; J. 1847, 1291 ; 1849,

813; 1851, 865; 1852, 958-961; Sharples, l.c.; Moseley, Quart. Journ. Microscop. Sci. xvii. 1877; also Max Bauer, Edelsteinkunde, 2nd ed. 1909, Eng. trans. Precious Stones, I. J. Spencer, 1904.

It is now known that the materials constituting coral-reefs sometimes undergo remarkable chemical changes, and that the calcium carbonate is largely replaced by magnesium carbonate or calcium phosphate. In 1846 J. D. Dana and B. Silliman showed that the rock of an upraised coral-reef in the Pacific contained as much as 38 p.c. of magnesium carbonate. The deep boring made in the Atoll of Funafuti in 1897-8, yielded a series of cores, of which a chemical examination was made by E. W. Skeats and Hart Smith in the laboratories of the Royal College of Science. It was found that down to the depth of 637 feet dolomitization had only gone on to a small extent, the proportion of magnesium carbonate never exceeding 16 p.c.; but the lower portions of the core were very rich in the magnesium salt, containing from 30 to 43 p.c., the rock thus becoming almost a true dolomite. A large collection of coral limestones obtained by Alex. Agassiz, from reefs in the Pacific, was subsequently examined by Skeats, who showed that they contained varying amounts of magnesium carbonate up to nearly 42 p.c. Specimens from Christmas Island in the Indian Ocean gave similar varying results, percentages of magnesium carbonate up to over 43 p.c. being found. A coral limestone obtained by boring at Key West, Florida, yielded to G. Stieger, in the laboratories of the U.S. Geological Survey, over 14 p.c. of magnesium carbonate.

Coral reefs that have been covered by deposits of guano are found to have their carbonates largely replaced by phosphates. Thus the rocks of the coral reef known as Christmas Island in the Indian Ocean have been largely worked for the deposits of calcium phosphate, and Teall has shown that Clipperton Atoll in the North Pacific contains rocks with as much as 38½ p.c. of phosphoric acid.

(For changes in the chemical composition of coral rock, see Dana and Silliman, Amer. J. Sci. 2, i. 1846, 189; Judd, Chemical Examination of Materials from Funafuti in 'the Atoll of Funafuti,' Phil. Trans 1904, 362-389; Skeats, The Chemical Composition of Limestones from Upraised Coral Islands, Bull. Mus. Comp. Zool. Harvard, xlii. 1903, 53-126; Teall, Quart. Journ. Geol. Soc. liv. 1898, 230-232.)

CORALLIN, CORALLINPHTHALIN. PHENOLCORALLIN v. AURIN.

CORDIALS and **LIQUEURS** are spirituous compounds flavoured with essences obtained from fruits, herbs, spices, or other substances, usually sweetened with sugar or glycerol, and often strongly coloured. They are manufactured and used to a much greater extent in France and other European countries than in the United Kingdom, and although there is no essential difference between them, the term ' cordials ' is by many restricted to British, and ' liqueurs ' to the foreign preparations.

The spirit in the best qualities of liqueur is derived from the grape, but grain and other spirit is frequently employed, especially in cordials; but, whatever the origin of the spirit,

it should be highly rectified and neutral in character, so as not to impair the flavour of the finished product. The alcoholic strength of cordials and liqueurs varies greatly, but, on the average, they contain from 30 to 40 p.c. of alcohol, or 50 to 70 p.c. of proof spirit. The sugar must be pure, and is added in the form of a clear syrup.

The principal flavouring ingredients employed are (a) those used solely on account of their essential oils, as aniseed, bitter almonds, caraway, juniper berries, mint, lemon-peel, orange blossom, &c; (b) those valued for their bitter principles as well as their essential oils, as cinnamon, cloves, curaçoa apples (a kind of orange), gentian, ginger, orange-peel, sweet calamus, wormwood, vanilla, &c.; and (c) fruits, chiefly cherries, pineapples, raspberries, and strawberries. The flavourings are obtained either by digesting the flavouring ingredients (bruised or cut up) with alcohol and distilling the mixture to obtain an essence; or by filtering the alcoholic extract to form a tincture, or by simply expressing and clearing the juice of fruits or digesting the latter for a more or less prolonged period in spirit.

Artificial essences simulating the above flavourings are frequently employed, but their use in beverages is questionable, since it seems probable that their physiological action differs from that of the natural flavouring substances which they are intended to imitate.

The colouring matters most commonly used are as follows: Red, aniline red, brazilwood, cochineal, cudbear, and sandalwood; yellow, saffron and turmeric; blue, indigo; green, chlorophyll (from nettles, parsley, spinach, &c.) and mixtures of blue and yellow colourings; violet, aniline violet; and brown, a solution of burnt sugar or caramel (v. LIQUEURS).

J. C.

CORDIERITE v. IOLITE.

CORDITE v. EXPLOSIVES.

CORDYLITE (or **Barium-parisite**). Carbonate and fluoride of cerium-metals and barium (CeF)₂Ba(CO₃)₂, containing Ce₂O₃, 23·72, and (La,Di)₂O₃, 25·67 p.c. It occurs as small, pale wax-yellow, club-shaped hexagonal crystals in syenite-pegmatite at Narsarsuk near Julianehaab in south Greenland; sp.gr. 4·31. It is isomorphous with, and closely related to, parisite.

L. J. S.

COREINE v. OXAZINE COLOURING MATTERS.

CORIANDER FRUIT, Coriandri fructus, B.P. The dried ripe fruit of Coriandrum sativum (Linn.).

CORIANDER, OIL OF, v. OILS, ESSENTIAL.

CORIARIA MYRTIFOLIA v. SUMACH.

CORINDITE. A refractory and abrasive substance obtained by heating a mixture of bauxite and anthracite in a cupola furnace. Aluminium carbide is first formed and is ultimately transformed into a vesicular fused mass of crystalline alumina of high melting-point, low thermal expansibility, and great hardness, suitable for the manufacture of fire bricks for rotary cement kilns, gas and heavy oil ovens, coke ovens, &c.

CORIOFLAVINE v. ACRIDINE DYESTUFFS.

CORIOPHOSPHINES v. ACRIDINE DYESTUFFS.

CORK. Cork is derived from the bark of two evergreen species of oak tree, the cork oak,

Quercus suber (Linn.) and *Q. occidentalis* (Gay). The former yields the best cork, and grows mostly in those countries bordering on the Mediterranean up to the 45° lat. The latter occurs on the Atlantic seaboard of Portugal, Spain, and France up to 48° lat.

The cork tree is from 30 to 60 feet high, and 3-4 feet thick. It grows slowly and reaches the age of 150-200 years. The tree has the peculiarity of throwing off its outer bark when it reaches a certain age, and then reproducing it. It is this that makes the cork industry possible. The chief countries in which cork is produced are:

1. *Spain.* Particularly the province of Catalonia. Here the best cork is grown. Seville is the chief market.

2. *Portugal* Centres : Lisbon and Oporto.

3. *Algeria.* Here the cork trees form great forests ; those belonging to the State were some years ago fully 600,000 acres in extent

4 *Southern France* and the *Pyrenean district.* Large forests of *Q. suber* exist in the more mountainous parts, but in the low-lying 'Landes' the tree is *Q. occidentalis*, which grows as far north as Belle Isle.

5. *The Adriatic coast.* Some is produced in the Austrian provinces, but it is of inferior quality.

6. *Sicily, Sardinia,* and *Corsica* also yield cork of good quality.

For an account of the cork industry in Sardinia, *see* J Chem Soc Ind. 1919, 38, 352 R. From U.S. Com. Rep July 25, 1919.

Speaking generally, the cork tree seems to thrive best on dry granitic and sandy soils, and not to do well in damp or limestone soils

The complete bark of the cork tree consists of two layers :

(1) The dry dead bark, comprising the epidermis and the cork proper, with the mesodermis.

(2) The green living skin which clothes the wood immediately under the dry bark. This may be looked upon as the active cork-producing layer, and contains bast fibres and the endodermis.

The epidermis on one-year-old twigs is green and smooth, but in the second year between it and the green under-skin irregular white waxy masses are formed ; these represent the beginning of the cork formation and increase from year to year, changing gradually into cork proper. At the end of the third year the epidermis dries up and cracks.

Barking the trees. This is the most important operation in the management of a cork forest, because on the care with which it is carried out depends the life of the trees and the regularity of the slabs produced.

. In barking, the workman takes a special tool and makes a cut round the stem above and below the portion of bark to be removed. A vertical cut or cuts are made so that the bark may be stripped off the tree, in which operation the shaft of the tool is used as a lever. Care must be taken not to bruise the green underskin, the real producer of the cork.

The first barking produces so-called ' virgin cork,' which is of little value, as it has not elasticity enough for use as bottle corks. It was formerly used for the production of Spanish

black, but of late years it has been employed in the manufacture of ground cork.

During the first year of growth the tree produces from 3 to 5 mm. of cork, but afterwards less, the mean for the first 9 years being about 2·1-3 mm., giving a total thickness of 20¾ mm. After 9 or 10 years, when barking usually occurs, the growth is slower, but where thicker cork is required, the period is of course longer. The first stripping usually takes place on the 15 20 year-old tree. The best cork is yielded by trees of from 50 to 100 years old. Those growing in the mountainous districts yield a smaller quantity but better quality of cork.

After the cork bark has been removed from the tree, it is stacked and weighted with heavy stones to flatten it, and when dry it is scraped with an iron tool to remove the epidermis The cork is then immersed for 5 or 6 minutes in a tank of boiling water, when it swells, and, according to the quality, retains this swelling more or less permanently. The water also removes tannin, vegetable acids, and their salts. In Spain the cork is occasionally passed through a fire, whereby it is superficially blackened, acquiring, it is supposed, by this treatment especially good qualities or ' nerve.'

After steeping, the plates are placed in heaps, weighted, and by hydraulic presses compressed into bales and bound with hoop iron.

Chemistry of cork. Cork extracted with hot water under pressure, yields gallic acid, colouring matters, iron and magnesium salts By extraction with alcohol it yields ' cerin,' or cork wax $C_{32}H_{26}O$. Siewert examined the alcoholic extract and isolated from it ' decaeryhe acid ' $C_{10}H_{18}O_2$.

The composition of cork has been further studied by Kugler (Arch. Pharm. 1884, 217) ; Gilson (*ibid.* 1890, 690) ; and Hy. Ingle (J. Soc. Chem. Ind. 1904, 1197).

Suberine, according to Kugler, is a real fat, which cannot be entirely extracted by solvents, because they do not penetrate the material sufficiently.

Gilson saponified cork from *Q suber* with 3 p.c. alcoholic potash, and isolated from the filtrate 44 p.c. of fatty acids, consisting of : *Phellonic acid* $C_{22}H_{32}O_2$, m.p. 95°-96°, a monobasic acid giving a violet colour with zinc chloride-iodine solution ; yield 8 p.c. *Suberinic acid* $C_{17}H_{30}O_3$, a semi-fluid sticky substance ; 36 p.c. *Phloionic acid* $C_{22}H_{40}O_7$: fine white needles, m.p. 120°-121° ; in small amount.

Gilson considers suberine not to be a true fat, but rather a mixture of complex esters and possibly condensation products of different acids.

Treated with iodine solutions cork does not give the cellulose reaction, and there is some dispute as to whether cellulose or a pentosan is the carbohydrate present in cork. Gilson, from microscopic examination, considers that cellulose is present.

. Cork also contains certain aromatic compounds, tannin and the aromatic aldehyde of wood, hadromal, besides coniferin and vanillin.

Treated with strong nitric acid, cork produces suberic acid $(CH_2)_6(COOH)_2$, oxalic acid, and other products. Strong sulphuric acid chars it, but it is little affected by hydrochloric acid. Chlorine, bromine, and iodine cause cork to shrink, the two former first bleaching it. Ignited

it burns, swells up, and forms a charcoal called Spanish black.

Physical properties.—The sp.gr. of cork is variously given from 0·12 (Rollmann) to 0·24 (Muschenbroek); on the average 0·16.

The uses of cork depend on its compressibility, elasticity, imperviousness to liquids, its lightness, its stability to weathering, &c. It is used in making stoppers, mats, soles, linings, springs for heavy waggons, as anti-vibratory and sound-deadening materials.

Waste cork is granulated by suitable machinery, sifted, and then ground to powder. The finest dust is mainly used in the manufacture of linoleum. Slightly coarser cork is used for the manufacture of cork carpet, but in both cases the binding material is prepared linseed oil.

Still coarser cork, of the size of peas, mixed with a proportion of lime, is employed in the manufacture of mats, insulating materials for water and steam pipes and cold storage chambers, packing, artificial corks for bottles, &c

In order to bind the particles of cork together are employed (1) collodion; used for bath mats and stoppers. The granulated cork of various grades in suitable proportions is mixed with the solution and the pasty mass pressed into perforated moulds; these are then heated in a suitable chamber provided with a condensing appliance to recover the solvents, ether and alcohol. 'Suberite' belongs to this class. The mat is removed from the mould and 'buffed' (sand-papered) on a buffing machine similar to that used by cabinet makers. Cork stoppers are made in a similar manner, and also insulating slabs and tubes for covering steam and water pipes.

(2) Gluten casein, and glue mixed with oily materials and resins and dissolved in suitable solvents, after mixing with the cork (rendered more or less insoluble by means of formalin, tannin, dichromates, lime, &c.), have also been used and patented for the production of cork slabs, &c., from granulated cork The cork of various degrees of fineness is mixed with the cement, subjected to powerful hydraulic pressure in moulds, and in some cases heated up to 200° to harden the albuminous matters of the cement.

(3) Mixtures of cork with silicate of soda and barytes or other pigment have been used for steam-pipe coverings

Slabs of cork have also been made by soaking cork in soap solutions, then drying, treating with milk of lime, again drying and pressing the resultant mass into heated moulds.

Another use for cork waste, more or less finely ground, is in the production of floors In this operation ground cork is mixed with a cement, such as Portland cement, or more often a mixture of cork and calcined magnesia is mixed with a solution of magnesium chloride and the pasty mass spread on the floor and allowed to harden; other salts, such as lead acetate, are sometimes added.

Cork dust is also used as a packing for the hollow spaces between the walls of cold-storage chambers, round the pipes of ice plants, &c., no binding materials being employed. Mixed with pitch, granulated cork is used as the filling between the outer and inner soles of boots,

especially American. It forms a warm, water-proof and resilient layer.

Granulated cork of various degrees of fineness is also mixed with the paint used to coat iron surfaces where there is danger of the condensation of moisture, such as in the cabins of steamers, in breweries, factories, laundries, and the like.

Hy. I.

CORNISH CLAY *v.* CLAY.

CORNISH STONE *v.* CLAY and CHINA STONE.

CORN OIL *v* MAIZE OIL.

CORNUTINE *v* ERGOT

CORONITE. An explosive consisting of nitroglycerine, 38–40 parts; nitro-cotton, 1-1½ parts; ammonium nitrate, 26–28 parts; potassium nitrate, 3-5 parts; aluminium stearate, 11–14 parts, rye flour, 8–11 parts; wood meal, 2-4 parts; liquid paraffin, 2-4 parts (*v.* EXPLOSIVES)

COROZO. Vegetable ivory. The seeds of *Phytelephas macrocarpa*

CORROSION OF METALS. By the term 'corrosion' is generally understood the disintegration of a metal through oxidation Usually a skin of oxide is formed which more or less protects the underlying metal from attack. Copper, zinc, lead and aluminium are cases in point. Iron,[1] on the other hand, is exceptional, in that, when oxidised by exposure to ordinary atmospheric influences, a pulverulent, hygroscopic mass of oxide, known familiarly as rust, is produced, which not only fails to protect the underlying metal, but actually accelerates further corrosion. For this reason, and also because iron is of such enormous commercial importance, the various problems associated with the corrosion of iron have received wide consideration and been made the subject of numerous researches; only in very recent years have systematic attempts been made to investigate the corrosivity of the other commercial metals.

Corrosion of iron. It is impossible here to review or discuss the voluminous literature which has appeared on the subject during recent years, and for particulars, including bibliography, the reader is referred to Friend's Corrosion of Iron and Steel (Longmans and Co , 1911), and to The Corrosion and Preservation of Iron and Steel, by Cushman and Gardner (McGraw-Hill Book Co., New York, 1910). It will suffice here to give a short account of the questions at issue.

Conditions essential to the corrosion of iron.—Before passing on to consider the various theories that have been offered to account for the mechanism of corrosion, it is important to have a clear conception of a few of the fundamental facts. These may be briefly summarised as follows :—

1. Liquid water, alone, both at ordinary temperatures and at the boiling-point, is without any appreciable action upon iron. In the course of time the metal frequently becomes very slightly tarnished, but no trace of rust-formation can be detected.

2. Water vapour is without visible action upon iron at ordinary temperatures upwards to about 300°C. At 350°C., and somewhat above, tarnishing occurs owing to a superficial layer of ferrous oxide being produced. At still higher

[1] The word 'Iron' is, both here and in the sequel, used in its broadest sense to cover wrought iron, steel, and cast iron.

temperatures a protective layer of ferroso-ferric oxide is produced, which, however, is not rust.

3. Dry air or oxygen has no visible action upon iron at ordinary temperatures. It is not until the metal is raised to about 220°C. that a pale yellow tint is acquired, which, as the temperature rises, becomes successively straw-coloured, purple, and finally blue. These 'tempering' colours, as they are termed, are due to the formation of thin layers of oxide, and are consequently not produced *in vacuō* (Roberts, Trans. Inst. Mech. Eng. 1881, p. 710), but are produced in perfectly dry air, such as that obtained by prolonged desiccation over phosphorus pentoxide (Friend, J. Iron Steel Inst. 1909, ii. 172).

4. A mixture of water vapour and air is without action on iron at ordinary temperatures. This was demonstrated by Dunstan and his co-workers (Trans. Chem. Soc. 1905, 87, 1548), who further showed that if, under the above conditions, liquid water is allowed to condense on the surface of the metal corrosion proceeds rapidly

From the foregoing it is evident that the rusting of iron is not an example of direct aerial oxidation, but that the presence of both liquid water and air or oxygen is essential.

. *Theories of rusting.*—Now although all ordinary irons readily corrode when exposed to the combined action of distilled or natural waters and air, it is of considerable academic importance to inquire whether or not a pure specimen of iron will corrode when exposed to perfectly pure air and water. In 1888 Crum Brown (J. Iron Steel Inst. 1888, ii. 129) summarised briefly the most important facts then recorded on the corrosion of iron and supported, though he did not originate, the then current idea that the action is primarily the result of acid attack—the acid, in most cases of aerial oxidation, being carbonic. According to this theory the metal is first attacked by dissolved carbon dioxide (carbonic acid) giving ferrous carbonate, or bicarbonate, and hydrogen. The ferrous salt is then oxidised by atmospheric oxygen, and the basic ferric carbonate potentially formed is, in presence of water, converted into hydrated ferric oxide (rust). As the carbon dioxide is thus wholly eliminated at the end of the cycle, it may be supposed to renew its attack on the iron.

This theory received vigorous support from Moody, who proved by a very ingenious experiment (Proc. Chem. Soc. 1907, 23, 84) that rust is formed by the action of oxygen upon iron in solution and not by its action upon the metal itself. In other words, the rusting of iron is preceded by its solution. Moody further satisfied himself, as the result of a careful series of experiments (Trans. Chem. Soc. 1906, 89, 720), that water and oxygen alone are quite insufficient to induce rusting. In experiments where iron had remained bright for many weeks in contact with pure air and water, the introduction of a minute quantity of carbon dioxide at once determined rusting. The experiments of Friend (J. Iron and Steel Inst. 1908, ii. 16 ; Proc. Chem. Soc. 1910, 26, 179) led to the same conclusion.

On the other hand, Whitney, in 1903 (J. Amer. Chem. Soc. 25, 394), applying modern electrochemical theory to the process, expounded the diametrically opposite view that water and air alone suffice to establish rusting. According to modern views, the action of an acid on a metal is ascribed to an exchange of electric charges between the hydrogen ions of the acid and the electrically neutral atoms of the metal, the hydrogen being deposited on the metal in the molecular state, and the metal atoms passing into the solution as metal ions. Inasmuch as pure water is regarded as being to some small extent ionised into hydrogen ions and hydroxyl ions, it is to that extent, electrochemically speaking, an acid, and when iron is immersed in it, there should be a deposition of hydrogen on the iron and an equivalent formation of iron ions. The water round the iron now contains ferrous ions and hydroxyl ions, or in other words, is a dilute solution of ferrous hydroxide. If oxygen has access to the ferrous hydroxide solution, hydrated ferric oxide will be formed and deposited as rust.

Such in outline is Whitney's theory, apart from the detailed application of Nernst's theory of electrolytic solution pressure, which he also introduces. The explanation just given for the action of pure water on pure and physically homogeneous iron, involves the deposition of hydrogen as a film of gas on the immersed portion of the metal. As this film would prevent further contact between the metal and the water, it is supposed that it slowly dissolves in the water and escapes by diffusion, or is oxidised by the dissolved oxygen, so enabling the action to continue. This theory received considerable support from W. H. Walker and his co-workers (J. Amer. Chem. Soc. 1907, 29, 1251), who concluded that they had 'substantiated the work of Whitney, and shown that iron does dissolve in pure water in the absence of carbon dioxide and oxygen.'

Dunstan, Jowett, and Goulding (Trans. Chem. Soc. 1905, 87, 1548).

It may be added, in passing, that the names of Cushman (The Corrosion of Iron, Bulletin No. 30, U.S. Dept of Agric. 1907), Tilden (Trans. Chem. Soc. 1908, 93, 1358), and of Heyn and Bauer (Mitt. Königl. Material-prüfungsamt, 1908, 26), must be added to those who believe that iron will corrode in the presence of pure water and oxygen.

Nearly all the experiments just referred to were carried out with iron of ordinary commercial purity. This circumstance made it possible for supporters of the 'acid theory' to ascribe the rusting in absence of carbonic acid, to the presence of acidic substances generated from impurities in the iron itself. Lambert and Thomson (Trans. Chem. Soc. 1910, 97, 2426) found that carefully purified iron remained unchanged when exposed for several months to purified air and water. Any specimen of commercial iron, or of iron prepared with fewer precautions than the immune sample, rusted quite readily in the same circumstances. From their experiments, the authors concluded that whilst pure iron will not rust in pure air and pure water, iron will do so if it contains only a small amount of impurity, even if the impurity is neither acid in itself nor likely to give rise to acid.

From the foregoing it is evident that opinions widely differ as to the chemistry of corrosion. Academically, therefore, the problem still awaits solution. In actual commercial practice, however,

since neither water, air nor iron itself, is ever quite pure, it may be safely postulated that corrosion will result whenever these three are brought into contact.

The Mechanism of Corrosion.—Aitchison (J. Iron and Steel Inst., 1916, I., 77) has outlined an attractive theory according to which, in the case of a perfectly annealed specimen of pure iron, a difference of potential exists between the crystals of ferrite and the amorphous, inter-crystalline material, thereby leading to corrosion. Any potential difference between the crystal grains themselves, due to strain, in a less perfectly annealed specimen will add to this effect, the total corrosion being the sum of the two actions. In the case of iron containing carbide the main differences of potential will be between the carbide and ferrite, the latter functioning anodically and ₐoxidising away. The case of steels containing alloying metals is interesting. Potential difference exists between the carbide and solid solution, the latter acting as anode. If the alloying element is associated entirely with the carbides, as in the case of small quantities of W, V, and Mo, they do not decrease corrosion. Ni, on the other hand, enters the solid solution, reducing its solution pressure and hence the potential difference between it and the carbide, thus hindering corrosion.

The ferroxyl indicator The study of the susceptibility of iron to rust, and especially of the localisation of susceptibility, has been aided considerably by a device due to Cushman (l c, and J. Iron and Steel Inst. 1909, I. 33) and Walker (J. Amer. Chem. Soc. 1907, 29, 1257) The iron to be studied is fixed in a jelly made of agar-agar, in which small quantities of phenol-phthalein and potassium ferricyanide have been incorporated. Wherever the iron is being attacked, blue ferrous ferricyanide (Turnbull's blue) appears, whilst the second electrode in the circuit declares itself by the pink colour developed from the phenol-phthalein. The pink colour indicates the presence of hydroxyl ions.

The chemical nature of rust.—Rust is a pulverulent, hygroscopic mass, ranging in colour from brown to red, and consisting of iron oxidised more or less completely to hydrated ferric oxide. As a rule, the browner the rust the greater is the extent of hydration. Some ferrous oxide is generally present also, particularly if the original metal has not been completely oxidised away. This ferrous oxide has a blackish appearance and may be found in the innermost layers close to the metal (*see* analyses by Moody, Trans. Chem. Soc. 1906, 89, 726 ; Tilden, *ibid.* 1908, 93, 1358 ; Gaines, Chem. News, 1910, 101, 205 ; Steel, J. Soc. Chem. Ind. 1910, 29, 1141, &c.). Rust also contains free water in addition to that chemically combined with it, and it readily absorbs carbon dioxide from the air. These two properties serve to render it an active stimulator of corrosion, for the carbon dioxide dissolves in the moisture yielding carbonic acid. This attacks a portion of the iron converting it into ferrous carbonate, which in turn is oxidised by the air to rust. The liberated carbon dioxide is now free to attack further portions of iron in a similar manner.

Graphitisation is a form of corrosion to which cast iron is particularly liable, the mass becoming so soft as to be readily cut with a knife. The metallic iron is more or less completely oxidised, mainly to ferrous oxide. Frequently portions of this latter have been washed or dissolved away, the remainder collecting within the pores of the now isolated mass of graphite. Examples are afforded by Berzelius (Traité de Chimie, 1831, vol. iii.), Rennie (Min. Proc. Inst. Civil Eng. 1845, 4, 323), Draper (Chem. News, 1887, 56, 251), Le Naour (J. Iron Steel Inst. 1898, I. 526), Holgate (Gas World, 1913, 58, 479), and others. Of these Berzelius drew attention to the cast-iron cannon balls raised at Karlskrona from a ship that had been sunk fifty years previously. They had been converted into a soft, porous mass which spontaneously heated upon exposure to air. Rennie mentions the case of cast-iron guns reclaimed from the sea in 1822, off Holyhead, after an immersion of about 100 years. When brought out of the water they were quite soft, but upon exposure to the air, they hardened to such an extent that they were used to fire salutes when King George IV. passed through Holyhead on his way to Dublin. It was observed that these old guns gave louder reports than any others. As a rule, this kind of corrosion does not take place with the purer forms of commercial iron, although a few cases of similar softening are on record where wrought iron has been subjected to prolonged immersion in sea water (Lidy, Engineering News, 1897, 39, 85). The percentage of carbon in such cases is, of course, much less than with cast iron, but is frequently much higher than the normal in consequence of the solution and removal of some of the iron.

Influence of dissolved substances on rusting. The effect of dissolved salts in the water has received great attention in both the laboratory and industrial study of rusting.

As a general rule, a dissolved salt might be expected to stimulate corrosion by increasing the conductivity of the water. If the substance gives an acid solution this action will be all the more marked. On the other hand, concentrated salt solutions do not dissolve oxygen to the same extent as pure water, so that if the metal is completely immersed, retardation of rusting might be expected on this account. The above conclusions are borne out by the experimental work which has been done Acids and ammonium salts stimulate corrosion very considerably ; sodium chloride stimulates in dilute solutions and retards in concentrated solutions. Generally speaking, as the concentration is increased the corrosivity increases to a maximum (critical concentration), and then, unless interrupted by saturation of the solution, falls practically to zero (limiting concentration). The limiting concentration in certain cases is found to have an extremely low value, *e.g.* in alkaline solutions and in chromates and dichromates. Chromates and dichromates, and other oxidising agents are known to render iron passive, and Dunstan and Hill (*l.c.*) have shown that alkalis also produce passivity, so that the effects may all be due to this cause. In any case there is no doubt that above a small concentration, many substances, such as potassium and sodium carbonates, permanganates, iodates, chromates, and dichromates, borax, &c., will prevent rusting entirely. This property of

the chromates is beginning to find industrial application in the painting of iron work, and the protection of boilers. When more than one electrolyte is present in the water the effects are more complicated and it is found that the concentration of the inhibitor must usually be considerably greater than when it is present alone, if corrosion is to be prevented. An interesting special case is the behaviour of potassium dichromate in the presence of other salts. In such cases the dichromate being an acid salt reacts with the other salt to produce free acid, which destroys the passivity and allows rusting unless the dichromate is in large excess. For practical application as a rust preventive in such cases, potassium chromate which produces no acid is equally effective (Friend and Brown, J. Iron and Steel Inst. 1911, I. 125).

The temperature of a solution exerts an important influence upon its relative corrosivity. A 3 p.c. solution of sodium chloride at 10°C. is considerably more corrosive than tap water at the same temperature, but as the temperature rises the relative corrosivity falls, until at 21°C the solution is appreciably less corrosive than tap water. The behaviour of sea water, which contains approximately 3 p.c. of sodium chloride, is of practical interest to the engineer. At 11°C. it is considerably more corrosive than fresh water; at 13°C. the two waters act similarly; whilst at all higher temperatures sea water is less corrosive than tap water (Friend and Brown, Trans. Chem. Soc. 1911, 99, 1302). In the western part of the tropical Pacific Ocean a temperature of 32°C. is frequently attained; whilst in the Red Sea and Persian Gulf temperatures of 34·4°C. and 35·5°C. respectively have been recorded. Such waters, therefore, are much less corrosive than river waters at the same temperature. In the Arctic Ocean, on the other hand, the temperature often lies below 0°C., and such waters are much more corrosive than fresh waters. Between these two extremes all grades of temperature occur with corresponding fluctuations in the relative corrosivities.

It is a matter of common knowledge that alkalis, if present in sufficient quantity in solution, will completely inhibit corrosion. The merest traces of sodium or potassium hydroxide will suffice to do this provided the solution is protected from neutralisation by the carbon dioxide of the air. Upon exposure to the ordinary atmosphere, however, carbonates are produced, and these tend to stimulate corrosion at ordinary temperature unless the concentration of the alkali hydroxide is sufficiently great to yield at least the limiting concentration of alkali carbonate, namely, a 0·25 p.c. solution. An interesting case arises when iron is immersed in alkaline solutions containing dissolved inorganic salts. For example, iron will remain untarnished for an indefinite period in a 1 p.c. solution of potassium hydroxide. Upon addition of potassium chloride however, corrosion is readily induced. It is possible, however, to increase the concentration of the alkali to such an extent that corrosion is entirely inhibited, no matter what concentration of chloride be added. The minimum amount of alkali required to inhibit corrosion varies with the nature of the added salt, and rises with the concentration of the same

until saturation of the last-named is reached. It is important to note that when iron corrodes in alkaline solution, the rust invariably takes the form of pitting, being localised at various points on the surface of the metal. When scraped away its interior is found to be dark, consisting largely of ferrous oxide, and the metal is observed to be eaten out or corroded into a small pit. The original cause of this pitting is probably the presence of traces of superficial impurity; nevertheless, even the purest forms of commercial iron, such as Kahlbaum's electrolytic metal, readily pit in this manner. This is a point of considerable importance to boiler engineers, inasmuch as alkaline feed waters are liable to produce serious trouble. It is not difficult to imagine that a large iron boiler or tank might very well lose several pounds in weight through a uniform superficial corrosion, and not be seriously injured thereby. Yet the loss of only half an ounce, if localised in the form of a deep pit passing entirely through the metal, might be disastrous. The remedy in such cases appears to be in raising the concentration of the alkali until the inhibiting point is reached.

Various factors influencing corrosion.—It has already been indicated that the concentration of dissolved oxygen at the surface of the metal has a very important influence on the progress of rusting. Practical experience confirms this in many ways. Pipe lines conveying water have been known to fail mainly on account of the extreme aeration of the water. Bridge structures always rust most readily near the water level, particularly if the water is in slight motion (*see* Cobb, J. Iron Steel Inst. 1911, I. 170). Iron work which is deeply immersed in water or deeply buried, rusts much more slowly than that which is nearer to the atmosphere. The oxygen used up at the metal-water surface, is gradually replaced by diffusion from the air-water surface, and anything which prevents or decreases the rate of diffusion, such as reduction in the size of air-water surface, or covering it with a layer of material impermeable to oxygen, will delay rusting. The rate of flow of the water past the metal might be expected to have, an influence in this respect, and Heyn and Bauer (Mitt. Königl. Material-prufungsämt, 1910, 28, 93) have actually found that slight motion increases the rate of corrosion for both cast iron and steel, especially the former. With an increased rate of flow, however, the corrosion decreased again. At high temperatures, it is naturally found that the tendency to rust is greatly increased although, under many conditions, this may be compensated for by the diminution in the supply of oxygen caused by the lower solubility.

Influence of physical condition.—It is an experimental fact that two samples of iron may possess precisely the same chemical composition and yet exhibit a marked difference in their powers of resisting corrosive influences. This is attributable to variation in the physical properties of the metals. A series of interesting experiments was carried out by Andrews (Min. Proc. Inst. Civil Eng. 1894, 118, 356) on this point, with the object of determining the influence of tensile, torsional and flexional stresses, respectively, upon corrosion. In so far as the first of these, namely, the tensile stress, was

concerned, it was found that the strained portion was cathodic to the unstrained when both were connected in a cell containing sodium chloride solution; in other words, the strained portion resisted corrosion more successfully than the unstrained. On the other hand, Hambuechen (Bull. Univ. Wisconsin, Eng. Ser. 8, 1900), after a similar series of experiments, was led to an opposite conclusion. This apparent discrepancy is explained by the work of Richards and Behr (Pub. Carnegie Inst., Washington, 1906), which makes it clear that any difference of potential existing between strained and unstrained portions of metal is very small and is greatly influenced in direction by local circumstances. Burgess (Trans. Amer. Electrochem. Soc. 1908, 13, 17) found that iron deformed by stretching beyond the elastic limit corrodes more rapidly than unstrained portions, and this is supported by the work of Heyn and Bauer (J. Iron Steel Inst. 1909, 1. 109). As regards the influence of torsional and flexional stress, Andrews found the unstrained portions to be more susceptible to corrosion than the strained. Here again the extent of the strain and the local conditions will each exert due influence upon the result

In 1911 Hanemann drew attention to some interesting effects produced by heat treatment upon the resistance of steel to acid attack (Stahl und Eisen, 1911, 31, 1365). He showed that each steel, according to its carbon content, appears to have an optimum quenching temperature, at which a maximum tensile strength is obtained. His results further indicated the existence of a close connection between the tensile strength and solubility of the steel, the steel with the highest tensile strength exhibiting the greatest solubility in acid. From the foregoing it is evident that the physical condition of the metal exerts an important influence upon its corrodibility.

Influence of chemical composition.—The chemical composition of iron or steel has an important bearing upon its resistance to corrosion. This is most marked in the case of cast iron and steel, since these have a wider range of composition than wrought iron. The most usual effects of alloying elements may be summarised as follows (Friend, Paper read before Staffs. Iron and Steel Inst. Feb. 21, 1914).

1. Some elements, such as sulphur, exist in steels in the form of relatively oxidisable compounds. In manganiferous and cupriferous steels the sulphur is present mainly as the sulphides of copper and manganese. These readily undergo oxidation to sulphureous acids which stimulate corrosion.

2. Not a few elements combine with iron forming alloys or compounds highly resistant to corrosion. Such appears to be the case with phosphorus, nickel, chromium, and silicon.

3. The presence of one element may tend to alter the chemical or physical condition of a second element present in the iron or steel. For example, silicon tends to throw the carbon out of combination with the iron, and effect its separation in the form of graphite. This is a well-known reaction in blast furnace practice, and the consequence is that the corrodibility of the metal is not only influenced by the presence of the silicon *per se*, but also by the altered condition of the carbon.

4. Alloying elements tend to produce segregation or unequal distribution of the components of the metal during solidification. Serious differences of potential are thereby initiated and the liability to corrode is proportionately enhanced.

In addition to lack of homogeneity in the metal itself it must be remembered that contact with a less electro-positive metal, the presence of small quantities of mill scale (Fe_3O_4), or even of rust itself, will cause the iron to become the soluble electrode in a galvanic circuit and thereby hasten its corrosion. It is therefore always advisable to avoid making contacts with other metals, or even with other kinds of iron, at points where electrolytic action might take place. The fact that iron in constant use does not corrode so fast as when at rest has been ascribed to the fact that any oxides formed are quickly removed and do not remain to exercise a galvanic influence.

Influence of carbon and manganese.—Two of the most important alloying elements in steel are carbon and manganese, and the influence of these upon the corrodibility of the metal has been made the subject of considerable study. Hadfield and Friend (J Iron Steel Inst. 1916, l. 48) summarised their results as follows :

1. The addition of carbon from 0 03 to 1·63 p.c. to pure iron containing less than 0·2 p.c. of manganese, results in a steadily increasing rate of corrosion both in tap water and in sea water : an initial fall in corrosion with a rapid rise to a maximum with 1 05 p.c. carbon in alternate wet and dry ; and a rapid rise in corrosion to a maximum with 0 8 p c carbon when exposed to the action of dilute sulphuric acid.

2 The addition of 0·7 p.c. of manganese to the above steels results in a slightly increased corrosion in tap water, sea water, and in alternate wet and dry tests, with a carbon content of up to about 0·4 to 0·6 p c. With higher carbon contents the manganese generally affords a slight protection, which is very decided in the wet and dry tests. On the other hand, the presence of the manganese enormously increases the solubility of the steels of all carbon contents in dilute sulphuric acid. This is a point of great commercial importance since in ordinary steels the manganese content is very liable to fluctuate between 0·2 and 0·7 p.c. and it is very evident that the latter are unsuited for acid atmospheres or liquors. For example, in large towns considerable quantities of sulphur acids are found in the atmosphere, owing to the combustion of bituminous coal, which, containing a small percentage of iron pyrites, leads to the formation of sulphur dioxide, and this dissolving in rain rapidly oxidises to sulphuric acid, giving the rain water an acid reaction. It has been shown that in the industrial quarters of a large manufacturing town this acidity will sometimes represent as much as 90 lbs. of sulphuric acid per acre per annum, whilst in the residential quarters it will probably not be more than about 25 lbs. The sulphuric acid, however dilute, coming in contact with iron-work, accelerates the rusting, and by its corrosive action renders more difficult the protection of the metal.

For such districts steels of very low manganese content would appear to be most suitable.

3 By increasing the manganese content to

2 p.c. upwards the corrodibility of the steels is greatly decreased in neutral media, although in dilute sulphuric acid the solubility is greatly enhanced.

Numerous other researches on the influence of carbon, nickel, chromium, copper, &c., have been carried out by Breuil, Chappell, Aitchison, Buch Diegel, and others, but for accounts of these the reader is referred to the J. Iron Steel Inst.

Relative corrodibilities of wrought iron and steel.—The question as to which of the two metals, wrought iron or steel, is the more resistant to corrosion is one which has attracted much attention. The subject has been discussed by several investigators (see Trans. Faraday Soc. 1916, 11, part 2), who point out that the mean result of examining a large number of samples of wrought iron and of steel after exposure to corroding influences indicates that the two metals are practically equally resistant. Nevertheless wide divergences exist between the different irons and steels in individual cases. This is not necessarily due to any irregularities in the metals themselves, but rather is it attributable to the fact that no one metal can be expected to offer an equal resistance to all kinds of corrosive influences The problem thus becomes one of determining which variety of iron or of steel is the most suitable for any particular purpose. It is conceivable that certain makes of wrought iron will prove most useful in certain circumstances, whilst under other conditions it will prove better to employ steel. Field tests, which are urgently needed to throw light upon these obscure problems, are in progress.

Corrosion of cast iron —Comparatively little research work has been published on the corrosion of cast iron. In 1883 Gruner found that cleaned cast iron was less attacked by air and moisture than wrought iron or steel (Compt rend. 1883, 96, 195), but was more readily attacked by dilute acids. This latter observation was confirmed in 1915 by Friend and Marshall (J. Iron Steel Inst. 1915, I. 353), working with a mild steel and grey cast iron In neutral corroding media there was little to choose between the two metals. The same investigators found (*ibid.* 1913, I. 382) also that a variation in the percentage of silicon between the limits of 1 2 and 2·3 p.c. exerts no influence *per se* upon the corrodibility of the metal. The fact that in many cases cast iron objects appear to have a longer life than corresponding ones in wrought iron or steel is attributable to the protection afforded by the outer skin formed on the cast iron during casting This may also account for the greater resistance offered by cast-iron pipes to the destructive action of stray electric currents (Brown, Electrical Engineer, New York, 1898, 26, 441).

Acceleration tests.—In order to determine what particular variety of iron or steel will resist corrosion most effectively many attempts have been made to employ rapid chemical tests in the laboratory. One of the most usual of these consists in immersing different samples of the metal in dilute sulphuric acid for definite intervals of time and noting the losses in weight. Those specimens that dissolve most readily are regarded as most readily corrodible. It cannot be too strongly emphasised, however, that such tests are of no general value whatever. The only reliable method consists in experimenting with the samples of metal under precisely similar conditions to those to which the metal will be exposed in practice. This, it is true, is a slow process, but the results are sure.

Prevention of rust.—Where the use to which iron is to be put does not admit of any protective coating, it is obviously necessary to consider all the above questions, with a view to providing conditions which shall keep corrosion as slow as possible. The steel plates of a steam boiler, for instance, are subjected to very stringent conditions which often cause extensive pitting, so that special attention has to be given both to the metal of which the boiler is contained and to the feed water. An example is described by Huntley (J. Soc. Chem. Ind. 1909, 28, 339) of remarkable corrosion in a stand-by boiler which could not be prevented by adding alkalis to the water. Blisters were found near the water level of the boiler, filled with a liquid which contained ferrous sulphate and sulphuric acid. The production of the sulphuric acid was found to be due to the presence of manganese sulphide in the steel. The blister of rust had retained the sulphuric acid, and oxygen passed in to oxidise the sulphide more rapidly than sodium hydroxide to neutralise the resulting acid. In this case, a remedy was effected by the addition of sodium arsenite, which presumably acted as a reducing agent combining with the dissolved oxygen. There are various other devices for the removal of oxygen, such as passing the feed water over scrap iron in a closed box, or the addition of an alkaline solution of tannin, which in the boiler forms strongly reducing pyrogallate. The use of dichromates or chromates has already been referred to, although the practice has not yet been widely tested on the large scale. Other attempts to protect iron have been made by placing pieces of zinc in contact with the metal so that the iron would be protected at the expense of the zinc. This practice is not very economical, and usually the effect of the zinc is confined to its immediate locality. In certain circumstances, however, the method is of value. A method of preventing or retarding the corrosion of boilers consists in applying an external current so that the boiler shell is the cathode, an immersed piece of wrought iron the anode, and the boiler-water the electrolyte. A current of 1 to 2 amperes at 4 to 8 volts' pressure is said to show a satisfactory reduction in the extent of the attack on the plates (Harker and Macnamara, J. Soc. Chem. Ind. 1910, 22, 1286).

Where conditions permit it, and especially in the case of structural iron work, it is of course a matter of economy to give to exposed iron work a protective coating. The first essential is to provide a coating which shall be as impervious as possible to air and water. Further considerations arise, particularly with regard to the course of events at points where the coating has given way. For small articles a film of vaseline, black lead, or similar material which can be readily renewed is of great practical value. A coating of hot tar or pitch (Angus Smith) has also found wide application. Wire and articles of sheet metal may be protected by means of a coating of a less corrodible metal,

usually zinc or tin. Tin plate finds its widest application in the manufacture of vessels to contain foodstuffs, and other articles for which a long life is not desired. It is less suitable for severe conditions, since at any point where the iron has become exposed a couple is produced in which the more electro-positive iron acts as the soluble electrode and suffers rapid corrosion. It is therefore of importance that the tin should be as free from pinholes as possible, and the ferroxyl indicator applied in a thin layer to the surface of the metal is a very valuable indication of the extent to which they exist. Every pinhole is indicated by the development of a blue spot which shows that iron is passing into solution. In galvanised or zinc-coated iron the state of affairs is reversed. The zinc protects the iron first by its own resistance to corrosion, and then when the coating is broken, by the fact that the iron is protected at the expense of the more electro-positive zinc. There are several methods now in use for providing the zinc coating in the most suitable form. In the hot dip method the iron, after passing through a 'fluxing solution,' is dipped into molten zinc. The fluxing solution which has for its object the cleaning of the iron surface usually contains hydrochloric acid, and the traces of this which are carried over often have an undesirable effect in producing corrosion of the finished product. In addition to the care necessary to avoid this effect, it is very important to control the bath so that a sufficiently uniform and thick layer of zinc shall be produced on the iron. Other methods of depositing the zinc are by electrolysis and by exposure to the vapour of zinc (Sherardising), and it is claimed that both these methods produce a more resistant coating than the hot dip process. The uniformity of a zinc coating can be tested by dipping the metal in a hot concentrated solution of caustic soda (Walker, Proc. Amer. Soc., Testing Materials, 1909, 8, 430). Pure zinc, under such conditions, is practically unaffected, but in contact with iron, as it would be where there were cracks or pinholes in the coating, a current of hydrogen is produced from the iron. Tested in this way, hot galvanised iron was found by Walker to be relatively free from imperfections, but wet or electrolytically galvanised was frequently porous, indicating the necessity for careful supervision of the rate of deposition of the zinc so as to obtain the most adherent coating. A number of other protective devices, mostly patented, depend upon the production from the iron itself of a resistant surface layer. The best known of these is the Barff-Bower method of producing a fine closely adhering layer of magnetic oxide, by the action of steam on the heated metal. In this way a very uniform and durable coating can be obtained on articles which are not too large. When the metal does become exposed, however, the oxide forms with the metal a couple which results in stimulated corrosion of the iron. In the Tatlock process, the magnetic oxide is obtained by heating in a bath of fused sodium or potassium nitrate. The Coslett process, which is largely used in bicycle manufacture, depends on the production of an insoluble layer of phosphate by the regulated action of phosphoric acid. These and similar methods of protection are all fairly efficient for

the protection of smaller articles or sheets of iron under not too stringent conditions. But where, as is often the case with structural and massive ironwork, the water may contain much soluble foreign matter (often of an acid nature), the progress of corrosion must be carefully watched and checked. This involves the use of a protective coat which shall be renewable *in situ* and easily applied. For this reason, a considerable amount of attention is now being paid to the protection of iron work by paint.

Paints usually consist of an intimate mixture of pigment and liquid vehicle. As regards the latter it is essential that it should excel in chemical permanence, imperviousness towards air and moisture, electric insulation, chemical inertness towards iron, resistance towards physical damage, elasticity, and finally in its drying, hardening or setting power. The vehicle most commonly in use is linseed oil, which, upon exposure to air, absorbs oxygen, being transformed into a tough, elastic solid called linoxyn. This oxidation proceeds only slowly in the case of the raw oil as obtained by pressure from linseed, and in order to facilitate the setting, a substance termed a drier is usually added, which, by some means not thoroughly understood, assists the oil to combine with the atmospheric oxygen. To the same end linseed oil is frequently heated, either in the absence of air or whilst a current of air is blown through; a drier may or may not be added in this case, according to circumstances.

The absorption of oxygen by the oil is at first accompanied by a slight expansion, amounting in the case of pure raw Calcutta oil to about 3 p.c. at 15°C. (Friend, Trans. Chem. Soc. 1917, 111, 162). Hence when thick layers of paint are exposed to the air the outer layer becomes oxidised most rapidly and by expanding causes the familiar crinkled appearance. For this reason the painter prefers to apply his paint in thin layers, so that, upon drying, a smooth and uniform coat results.

If the oxidation of the oil stopped at the formation of the solid linoxyn the paint film would be very permanent. Unfortunately such is not the case. Further oxidation takes place, although very slowly, water, carbon dioxide, and other products being evolved, and accompanied by a simultaneous contraction and embrittling of the film. In course of time the contraction becomes so great that the film cracks and peels away. Such old films are a source of danger to ironwork, inasmuch as they not only fail to protect the metal, but actually stimulate corrosion (Walker and Lewis, J. Ind. Eng. Chem. 1909, I. 754). Hence when cracking of the paint film has once begun it is desirable to scrape off the old paint and apply an entirely fresh coating. All the drying oils are open to this objection, and attempts have been made to utilise other liquid vehicles, such as nitrated cellulose in amyl acetate, &c.

The heating of linseed oil, referred to above, induces a certain amount of polymerisation, reducing its permeability to moisture and generally increasing its protective power when used in paint for iron work. Light greatly accelerates the setting of the oil, but unfortunately it also accelerates its subsequent decomposition; for this reason, other things being equal, the

most permanent paints are those containing black or red pigments, since these absorb the shorter rays of light and prevent them from hastening the destructive oxidation of the linoxyn. As regards the pigments, they should be in a fine state of division in order to admit of thorough incorporation with the oil. They should also be insoluble in water, and chemically both permanent and inert. The last-named property is largely dependent upon the solubility and in the case of certain pigments, such as the chromes, a very slight solubility in moisture is not altogether a disadvantage, since the dissolved chromate tends to inhibit corrosion, as already mentioned. This was found experimentally to be the case in the Atlantic City tests carried out under the ægis of Committee U of the American Society for Testing Materials. These tests were begun in 1908 and for details the reader is referred to Cushman and Gardner, Corrosion and Preservation of Iron and Steel (New York, 1910), and Gardner, Paint Technology and Paints (New York, 1911); suffice it to say, however, that paint mixtures containing chromates yielded promising results.

It is dangerous, however, to use pigments that are markedly soluble in water, since when these have dissolved out of the paint film by repeated rainfalls, pores are left through which moisture and air readily pass to the metallic surface beneath, leading to serious corrosion.

The chief functions of a pigment consist in (1) offering a support to the linoxyn, thereby affording a harder and tougher film, proportionately more resistant to mechanical injury; (2) reducing the permeability of the paint film to air and moisture, since the pigmentary particles are themselves impervious to these (There are other functions, but for further details reference may be made to Friend, Iron and Steel Institute Carnegie Memoir, 1918.) In the case of aerial iron work, a thick coat of paint protects the underlying metal from attack more efficiently than a thin coat, provided the thick coat is not so heavily laid on as to cause crinkling or running. The best results are obtained by multiple coats, two thin coats being more efficient than one thick one of equal weight. The iron structures should be painted whilst the scale is still on after loosely adherent flakes and rust have been scraped off. In this case the paint will last rather longer than if applied to the pickled or sandblasted surface and the labour of removing the scale is saved. Rust need not be so carefully removed prior to painting as was formerly believed to be necessary.

A useful paint for structural iron work not exposed to sea-water consists of oil with red lead, Indian red and lamp black, the three pigments being in approximately equal proportions by weight.

Almost equally good as the red or white lead paints for protection is a bituminous paint made from pitch, the distillation of which has not been carried too far. This must be absolutely free from free carbon and tar acids or ammonium salts, and if applied hot to the structure to be protected, gives very good results, the colour being the main drawback.

There are many circumstances in which such a bituminous paint is preferable to an oil paint, as, for instance, in gas works, urinals, or slaughter houses, where there is much ammonia in the air, which has an extraordinarily destructive effect upon oil paints.

Corrosion of iron in concrete.—In view of the widespread use of concrete reinforced with iron or steel the question of the corrosion of the metal in these circumstances is fraught with unusual importance. Owing to the fact that iron, upon rusting, undergoes considerable expansion (Bauermann, J. Iron Steel Inst. 1888, II 135), it follows that should corrosion of the metal occur when it is embedded in concrete, a cracking of the latter becomes inevitable, more air and water enter, so that corrosion proceeds with an increased rapidity and the structure becomes proportionately weakened. If the concrete is well made and the whole is undisturbed by stray electric currents it would appear that ferro-concrete structures may last almost indefinitely. The ingredients of the concrete should not be too coarse, otherwise thorough mixing and good contact will hardly be possible. The mixture must be well punned into position in order to eliminate voids in so far as is possible. A sufficient thickness of concrete should be applied, since, if it is too thin, it may crack mechanically and thus admit air and water to the metal. Substances likely to contain acids or acid producing constituents should be avoided, such as, for example, coke breeze and slags, which frequently contain dangerous sulphur compounds (*see* Report of Science Standing Committee of Concrete Inst. Mar 9. 1911 Friend, Trans Concrete Inst. 1917 18, vol IX.).

Concrete may be advantageously coated with some waterproofing material to render it still more impervious, provided such proofing is entirely free from acid or acid producing substances. This course is specially to be recommended in the case of reinforced concrete structures exposed to the action of sea-water, since the salt exerts a deteriorating effect upon the concrete. For this reason Creighton points out that if beach gravel is used in making the concrete it should first be very thoroughly washed to remove the salt, and furthermore salt should not be added to the concrete during building in cold weather to prevent its freezing (J. Franklin Inst., Nov. 1917.)

Corrosion of Non-Ferrous Metals.—The corrosion of non-ferrous metals has not been made the subject of so much study as that of iron and steel, nevertheless a considerable amount of useful information has been accumulated. The rare or precious metals, such as platinum, iridium, and gold, are so resistant to oxidation or corrosion at ordinary temperatures that they may be said, for all practical purposes, not to corrode at all. Nickel and cobalt are also very resistant to corrosion, although less so than the foregoing metals. Silver tarnishes, particularly in contact with sulphur or sulphureous substances, and is readily pitted or corroded by chlorides such as common salt. Mercury or quicksilver likewise tarnishes upon exposure to air, but the layer of oxide tends to protect the underlying metal from attack, if the liquid is kept stationary. Pitting is, of course, an impossible phenomenon in the case of a liquid. This leaves us with the following commercial metals to consider, namely

aluminium, copper, lead, tin, and zinc, together with their alloys. Such metals as rhodium, ruthenium, &c., hardly concern us here, being rather of the nature of chemical curiosities than otherwise.

Aluminium.—The study of the corrosion of aluminium has acquired a considerably enhanced importance of late years owing to the ever-increasing use of this metal for air-craft, fittings of sea-going vessels, and for domestic culinary operations.

Aluminium tarnishes upon exposure to air, and the layer of oxide, adhering closely to the metal, affords good protection in temperate climes against further corrosion. In hot, tropical countries, where moisture is plentiful, the aluminium corrodes more rapidly, and the coating of oxide, although apparently continuous, may be minutely porous. Aluminium drinking vessels acquire a foul taste in such climates, probably owing to the absorptive properties of this porous oxide layer (Desch, Trans. Faraday Soc. 1916, 11, Part 2).

Aluminium is oxidised by prolonged contact with hot distilled water in the presence of air, the insoluble hydroxide being formed. Scala (Atti R. Accad. Lincei, 1913, 22, (1), 43, 95) concludes that this is mainly due to the presence of iron, which passes into pseudo solution in colloidal form as ferrous hydroxide and catalytically accelerates the oxidation of the aluminium.

The greater the purity of the metal, and the less its variation in homogeneity, the greater is the resistance of the metal towards corroding influences. Consequently annealed samples are more resistant than those which have not been so treated (Bailey, J. Inst. Metals, 1913, 9, 79). Organic acids, particularly when hot and in the presence of dissolved chlorides, act upon aluminium (Watson Smith, J. Soc. Chem. Ind 1904, 23, 475), whilst boiling with dilute sodium carbonate solution causes the formation of soluble sodium aluminate, from which the hydrated oxide of aluminium is precipitated on passage of carbon dioxide. Both pure and crude alcohol attack aluminium fairly readily, and are rendered turbid thereby (Karpinski, Z. Spiritus-industrie, 1912, 35, 660). Hydrogen peroxide in dilute solution readily effects the oxidation of the metal (Droste, Chem. Zeit. 1913, 37, 1317), as do also dilute solutions of ammonia, sodium hydroxide, and sodium carbonate respectively, in the cold (Hale and Foster, J. Soc. Chem. Ind. 1915, 34, 464).

Copper and its alloys.—Copper tarnishes upon exposure to moist air at ordinary temperatures, and the skin of oxide thus formed tends to protect the underlying metal from attack. Water alone does not appreciably affect copper, and the employment of this metal for kettles for boiling water for culinary purposes is quite safe. Copper differs from iron in that it does not decompose steam, even at red heat. Indeed, cupric oxide heated in steam is reduced to cuprous oxide. Nitric acid readily attacks copper, and the metal oxidises in contact with alkaline solutions. Dilute hydrochloric acid attacks copper in the cold more seriously than nitric or sulphuric acid under similar conditions (Hale and Foster). When embedded in damp concrete copper remains in excellent condition

(Gaines, J. Ind. Eng. Chem. 1913, 5, 766). Sulphur tarnishes copper, and organic acids gradually convert it into basic salts (*see* VERDIGRIS, &c.). Solutions of electrolytes such as sea-water, &c., also attack the metal. [See report of Corrosion Committee J. Inst. Metals, 1919, 21, 87.]

The corrosion of an alloy is usually a more complicated process than that of a single homogeneous element, since the different constituents in an alloy do not behave alike towards corroding media. Owing to the corrodibility of iron and steel various alloys of copper are used commercially on a large scale for special purposes, as, for example, in the manufacture of condenser tubes, millions of which are in use at any moment by the Admiralty. Consequently a study of the conditions under which corrosion takes place assumes a position of corresponding importance. During the last few years increased attention has been given to this subject, notably by the Institute of Metals, and for full details of the work carried out under their auspices, the reader is referred to Bengough's Reports to the Corrosion Committee, as published in the Journal of the Institute.

Much so-called corrosion of metal-work really consists of mechanical abrasion. For example, furnace gases carrying with them fine particles of solid material on passing through metal tubes tends to wear them away. This action is accentuated by the presence of chlorides or sulphur compounds, since these yield with the metal compounds less hard in character, and which are in consequence more easily abraded, or they may even give rise to volatile salts which readily disappear as vapour. This is a common source of trouble with copper and its alloys.

Brass is an alloy of copper and zinc, and the resistance offered by it to solutions of electrolytes has been studied by many investigators. The action of chlorides in particular has received attention, notably by Desch and White (J. Inst. Metals, 1913, 10, 305; 1914, 11, 235; J Soc. Chem. Ind. 1915, 34, 258), whose results may be briefly summarised as follows :¦ Corrosion of brass takes place mainly by dezincification, for although both copper and zinc are removed in solution, the proportion of the latter metal in solution and in the flocculent precipitate is much higher than in the alloy. Consequently a layer of metal is left, in which the percentage of zinc is much less than in the original alloy, and which has an open, spongy texture that readily yields to oxidation under the influence of air or dissolved oxygen. This explains the presence of the layer of cuprous oxide frequently observed on the corroded surface of brass tubes, and which is thus probably not of direct, but of secondary origin. The removal of zinc grains proceeds at first along the boundaries of crystal grains, and in such brasses as exhibit twinning (α-brasses) along the dividing planes between twin crystals.

The presence of iron in solid solution in brass accelerates the corrosion, but small quantities of lead up to 1 p.c. apparently do no serious harm (Brühl, J. Inst. Metals, 1911, 6, 302). With 2 p.c. lead a protective layer of basic salts is formed, which tends to retard further action (Desch).

2 o

An interesting example of corrosion is afforded by a condenser tube taken from a vessel on the Manchester Ship Canal, and described by Desch. The composition of the original metal was Cu, 72·72 ; Zn, 27·04 ; Fe, 0·15 ; and Pb, 0·09. Along the bottom of the tube the metal had been almost completely dezincified, and a transverse section showed that practically only spongy copper remained. At a somewhat higher level the spongy copper extended only partly through the metal, but the boundary between the copper and unaltered brass was perfectly clear.

Tin, as is well known, greatly enhances the resistance of brass to attack by sea-water, and for this reason bronzes are in considerable demand for marine work. The standard Admiralty alloy for condenser tubes contains Cu, 70 ; Zn, 29 ; Sn, 1 0. The protective influence of the tin appears to be largely mechanical, in that it forms in neutral or faintly alkaline solutions of electrolytes a tough adherent layer of basic salt, which can only be detached with difficulty.

The behaviour of bronzes towards acid solutions has been studied by Giohtti and Ceccarelli (Gazz. chim. ital. 1909, 39, ii. 557), who find that their susceptibility to acid attack is intimately associated with microscopical appearance.

When embedded in damp concrete (Games, J. Ind. Eng. Chem. 1913, 5, 766) both monel metal and manganese bronze appear to resist corrosion exceedingly well. Addition of phosphorus to bronzes increases their resistance to corrosion, and phosphor bronzes, which contain up to 1·75 p.c. of phosphorus, have proved very valuable in marine work

Alloys of copper and aluminium, such as those containing up to 10 p.c. of the latter metal, have also proved very resistant to sea-water and dilute alkalies, a property that is further enhanced by the addition of nickel (Read and Greave, J. Inst. Metals, 1914, 11, 169), although, curiously enough, the nickel, if it has any action at all, tends to increase the corrodibility of the alloys in tap water, dilute mineral acids, and vinegar.

Lead.—(1) Pure Lead. The corrosion of lead of exceptional purity has been investigated by Lambert and Cullis (Trans. Chem. Soc. 1915, 107, 210). The metal, having been prepared in a high state of purity by the method of Stas (Bull. Acad. roy. Belg. 1860, 10, 295), was finally distilled *in vacuô* in quartz tubes at a temperature approximating to 1200° C. Its behaviour towards air, water, and a mixture of oxygen and water was then investigated. It was observed that, if the metal was exposed to air only a short time after distillation, its surface was quickly tarnished in the cold, indicative of slight superficial oxidation. If the metal, however, was kept *in vacuô* for several months, subsequent exposure to air did not cause any appreciable decrease of lustre for several days.

Other samples of freshly distilled lead underwent rapid corrosion upon exposure to pure water and oxygen. In the case of totally submerged specimens, white crystals of lead hydroxide were formed, together with a brown deposit, probably consisting of hydrated plumbous oxide $Pb_4O,2H_2O$. When the metal was only partially immersed in the water a bright yellow oxide was formed within half an hour of the admission of oxygen. The colour gradually turned to a dull red, the change requiring many months for completion, being accelerated by exposure to sunlight.

A sample of lead kept in contact with water for 12 months *in vacuô* presented an undiminished lustre, and no evidence was obtained in other experiments indicative of the slightest solubility of the metal under such conditions. Admission of pure oxygen led to no visible corrosion or tarnishing for more than a week, and even after six months oxidation had proceeded to such a slight extent that the layer of oxide was sufficiently attenuated to display interference colours.

From the foregoing it is evident that pure, distilled lead behaves somewhat differently towards air or aerated water, according to its 'age,' the specimens that have been most recently distilled proving more susceptible to corrosion than those that have had time to age, although the actual mechanism of the corrosion appears to be the same in either case. Most probably this is due to a difference in the physical character of the metal, and it is in accordance with the behaviour of other substances to suppose that the most unstable form or forms will predominate in the freshly distilled metal, thus giving it a heterogeneous character which gradually settles down to a homogeneous condition of maximum stability.

(2) Commercial Lead. Although commercial lead is a remarkably pure metal for technical and trade purposes, it cannot be compared with the distilled product of Lambert and Cullis It is important, therefore, to study its behaviour towards such corroding agents as are commonly met with in practice. This is particularly necessary, since the subject is intimately associated with the national health owing to the extensive employment of leaden pipes for the conveyance of potable waters to private dwellings.

The results obtained by early investigators are somewhat conflicting in many of their details (*see* Summary by Heap, J. Soc. Chem. Ind. 1913, 32, 771, 811, 847), but the following facts may be regarded as well established. Although Lambert found that pure water exerts no appreciable solvent action upon pure distilled lead in finite time, it is generally agreed that distilled water, freed from air by boiling, readily dissolves commercial lead, and even refined lead. Clowes (Proc. Chem. Soc. 1902, 18, 46) found that a sample of very pure lead dissolved to the extent of 0·3 gram per million parts of water, and according to Traube-Mengarini and Scala (Mem. R. Accad. Lincei, 1911, 8, 576), the dissolved metal is suspended in the water in colloidal form. Admission of oxygen converts the colloidal metal into colloidal hydrated oxide, the particles of which slowly aggregate to give a crystalline deposit, the liquid becoming turbid. Oxygenated waters are thus very corrosive towards lead.

The question now arises as to the influence exerted by atmospheric carbon dioxide upon the foregoing reactions. Water containing dissolved carbon dioxide has but little action upon lead in the absence of oxygen, and the presence of carbon dioxide in oxygenated waters reduces

their corrosive action by effecting the precipita-
tion of an insoluble carbonate of lead which
protects the metal from further attack. Thus,
for example, Graham (J. Soc. Chem. Ind. 1851,
4, 400) found that pyrophoric lead, which is
simply the metal in a state of exceedingly fine
subdivision, rapidly renders aerated waters
poisonous if carbon dioxide is not present, in
consequence of the formation and solution of
lead hydroxide, which is soluble to the extent
of 1 part of PbO in 10,000 parts of water
(Pleissner, Chem. Zentr. 1907. 11, 1055). The
presence of 3 p.c. of carbon dioxide, however,
prevents the water from becoming poisonous
owing to the formation of relatively insoluble
lead carbonate, 1 part of which requires 4 million
parts of water to effect its complete solution.
Lead is readily attacked by dilute nitric acid
in the cold, much less rapidly by hydrochloric
acid, and still less by sulphuric acid under like
conditions (Hale and Foster, J. Soc. Chem.
Ind 1915, 34, 464).

Yorke, in 1834, had already observed that
dissolved salts exert an important influence
upon the solubility of lead in waters. Of these
the most powerful inhibitors are phosphates,
such as those of the alkali metals, small quan-
tities of which almost entirely prevent the solu-
tion of lead. This is due to the formation of a
protective layer of lead phosphate which dis-
solves in water to the extent of only 1 part in
7 million parts of water. Carbonates and bi-
carbonates are also very effective, and it has
proved a useful procedure to pass certain
moorland waters through beds of chalk or
limestone to reduce their corrosivity. This
does not, in all cases, entirely prevent the solu-
tion of lead, since a mere trace of carbonate is
not sufficient for the purpose, 4 parts of CaCO₃
or MgCO₃ per 100,000 of water being required
as a minimum. Nevertheless, the procedure is
highly beneficial (Thresh, The Examination of
Waters and Water Supplies, Churchill, 1913 ;
Liverseege and Knapp, British Association,
Birmingham, Section B, 1913). Birmingham
water, which comes chiefly from Wales, is
treated at its source with powdered chalk for
the same purpose.

The foregoing offers an explanation of the
fact that waters which are temporarily hard
do not attack lead ; in other words, the lead
does not pass into solution continuously, since
a coat of insoluble carbonate is formed on its
surface. Permanently hard waters, on the
other hand, frequently attack lead rather
vigorously. Sodium silicate diminishes the
corrosivity of water. Dissolved nitrates, par-
ticularly ammonium nitrate, attack lead vigor-
ously ; but sulphates, chlorides, and acetates, as
a rule, much less so. Calcium oxide and
alkalis generally have a marked action ; and
damp concrete may produce serious corrosion
(Gaines, J. Ind. Eng. Chem. 1913, 5, 766). Pure
rain water and melted snow resemble distilled
water in their activity, but rain waters collected
in localities where macadam roads are in common
use are laden with calcareous dust, which reduces
their activity (Heap). Hence the first rain
water from such a district, after a spell of fine
weather, may have a comparatively slight action
on lead, whilst that which falls after the air has
been washed may be expected to act more

vigorously. On the other hand, rain water
collected in the neighbourhood of manufacturing
cities, is charged with nitrates, haloid salts, and
sulphur compounds resulting from the com-
bustion of coal, and may or may not be very
corrosive according to circumstances

The influence of organic matter upon the
solubility of lead in water is obscure. It is
generally believed that waters derived from
moorland and peaty sources are particularly
corrosive, and this is usually attributed to the
presence of peat acids or of carbon dioxide
(Thresh). Experiments carried out by Heap,
on the other hand, suggest that such waters,
though variable in activity, are considerably
less active than pure rain or distilled water.
Indeed, both distilled and rain water exhibited
in his tests less action on lead after contact
with peat, even although their acidity was in
some cases increased thereby. Water contain-
ing certain forms of organic matter yield,
after prolonged contact with lead, a floccuent
precipitate containing the metal and organic
material. This tends to deposit on the lead
surface and to form a loosely attached protective
layer (Heap).

Rise in temperature in general increases the
solubility of lead in water.

When sheet lead is immersed in a slightly
acid solution of lead nitrate or acetate it gradually
disintegrates, becoming loose in structure, and
ultimately is converted into a spongy crystalline
mass, owing to the metal having dissolved and
separated out again (see Heller, Zeitsch. physikal.
Chem. 1915, 89, 761 ; Cohen and Heldermann,
ibid. 733 ; Creighton, J Amer. Chem. Soc.
1915, 37, 2064). This phenomenon is character-
istic both of the purest assay foil and of commer-
cial lead (Desch), and possibly indicates the
existence of stable and metastable allotropes
(Cohen), the latter of which dissolves and
recrystallises as the former. Such a hypothesis
is, at any rate, in harmony with the observa-
tions of Lambert, to which reference has already
been made.

Lead antiques in museums frequently undergo
a gradual disintegration, being converted into a
white powder consisting essentially of lead
carbonate. In such cases chlorides are always
present in the powder (Matignon, Compt. rend.
1912, 154, 1619). Lead that has been immersed
in sea-water and dried so that crystals of salt
remain attached to the metal undergoes pro-
gressive destruction, for which the following
cycle of reactions is suggested :

$$2NaCl + Pb + O + CO_2 \rightarrow Na_2CO_3 + PbCl_2$$
$$\rightarrow PbCO_3 + 2NaCl$$
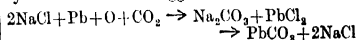
The sodium chloride thus acts as a catalyser,
and is able to effect, in the presence of air and
carbon dioxide, the disintegration of indefinite
quantities of lead.

Tin.—Metallic tin remains bright and
untarnished for long periods, both in dry and
in moist air, at ordinary temperatures. In a
piece of tin from an aboriginal cemetery in
Florida, Keller (J. Amer. Chem. Soc. 1917, 39,
2354) noticed a number of cavities lined with
small shining crystals, both in the form of thin
plates and acicular in shape. These consisted
of basic chloride SnCl₂.SnO. Water is practi-
cally without action upon tin both in the absence

of, and in the presence of, air. Tin is also very resistant to the action of dilute sulphuric and vegetable acids, and is thus exceedingly useful for protecting iron or steel from corrosion in the manufacture of articles required for culinary purposes. Caustic soda attacks it, but sodium carbonate, and particularly ammonia, are much less corrosive (Hale and Foster). When alloyed with copper or its alloys it greatly enhances their resistance to corrosion (*see* Bronze, above), and it exerts a powerful protective influence in other alloys, such as type metal (Meyer and Schuster, Zeitsch. angew. Chem 1914, 27, 12).

Zinc.—Ordinary commercial zinc readily oxidises in air, and is rapidly attacked by acids. Minute quantities of arsenic, antimony, copper, and tin, particularly the first two elements, accelerate the corrosion of the metal.

Zinc is largely used in the manufacture of galvanised iron, and waters passing through galvanised iron pipes or stored in galvanised iron tanks usually give a reaction for zinc. As a rule, however, this is not in sufficient quantities to be toxic.

Boiling water attacks zinc (Watson Smith, J. Soc. Chem. Ind. 1904, 23, 475), the hydrated oxide of the metal separating out. It is attacked by boiling solutions of sodium chloride, as also by hot dilute solutions of alkalis, such as sodium carbonate, zinc hydroxide being produced. The hydroxide does not form a protective layer in these cases, but, being readily detached from the metal, exposes fresh surfaces to attack. Dilute solutions of sodium hydroxide or ammonia corrode zinc in the cold, but sodium carbonate acts less vigorously (Hale and Foster. See also Report of Corrosion Committee J. Inst. Metals. 1919, 21, 59)   J. N F.

CORROSION, PROTECTION OF METALS FROM. Of the metals in common use iron (including steel) is not only the most corrodible, but because of its extensive and varied applications under widely diverse conditions, its protection from corrosion constitutes by far the most important case for consideration With the other common structural metals and their alloys corrosion has in some special cases to be provided against, as in the corrosion of condenser tubes, but, in general, copper, tin, lead, and zinc seldom need this attention.

In order to protect the surfaces of iron and steel structures methods based on several distinct principles are employed.

1. Exclusion of the agents causing corrosion : air, moisture, or water in the case of submerged structures.

This may be accomplished by :—

(*a*) Coating with an impervious oil film, or asphalt, pitch, &c.

(*b*) The use of paints, varnishes, &c.

(*c*) Coating with another metal not easily attacked by the corrosive agents.

2. By forming a non-corrodible skin consisting of some compound of the metal on its surface, such as the magnetic oxide (Bower-Barff process), phosphide, or nitride.

3. By the use of a substance which greatly reduces ('inhibits') corrosion.

4. Placing the iron in an electro-negative condition to another metal, so that the former is protected at the expense of the latter, or making the surface to be protected the cathode

(negative) and furnishing a continuous current from an external source.

It will be seen that there is a wide choice of methods, but practical considerations limit their application. In the case of large structures, ships, bridges, tanks, &c., the large surface, the fixed character of such structures, and the necessity for renewal of the protecting coat, determine the use of some form of paint or varnish paint. Deposition of another metal is applicable to a variety of conditions of use, ranging from the ordinary galvanising for tanks, roofing, &c., to electro-deposition of nickel, as in the case of bicycle parts. For small articles generally, processes of inhibiting, oiling, and formation of a surface compound are alternatives.

Before any system of protection can be properly applied it is essential that the metal surface shall be properly cleaned from dirt, mineral oil, rust (the ordinary ferric oxide Fe_2O_3), and mill scale (the black magnetic oxide Fe_3O_4) Plates from the rolling mills generally show patches of this oxide. Although it is an excellent protection against rusting when thinly and evenly covering the metal, patches of mill scale may set up active corrosion locally by galvanic action. Further, patches of scale are generally covered with fine cracks through which corrosive agents may pass, and the patch may scale off, carrying any protective composition with it, so that it is essential that all scale shall be removed before coating.

Rust and scale may be removed by mechanical means, scraping, wire brushing, and sand blasting, the latter being very efficient. Commonly they are removed by pickling the plates in sulphuric acid, 25 p c. In this acid red rust dissolves, and mill scale is thrown off by penetration of the acid, hydrogen being generated and forcing the scale from the plate. Arsenic in the acid is regarded by many as injurious. The plates should then be washed with water jets under fair pressure (if the plates are immersed in still water a 'gummy' film forms), and then steeped in hot milk of lime to neutralise any acid remaining.

Temporary protection from rusting is commonly done by smearing small articles with vaseline or heavy oil. Several processes of similar nature, have been patented, the principle of which is immersion of the metal at temperatures up to a red heat in various oils, and withdrawing while still hot, also spraying of metal hot from the rolls with oil. A layer of slaked lime pasted on is said to be more efficient than smearing with oil, and one patent has been granted for a paste of slaked lime made with a volatile solvent, like naphtha.

Asphaltic and coal-tar pitch compositions have great value as preservatives of iron and steel. For many purposes the black colour is prohibitive, but for buried pipes, &c., no better preservative can be employed. In 1848 Dr. Angus Smith took out his well-known patent covering the use of pitch. The pipes were preferably first heated, dipped in linseed oil, then heated to 300° F., and dipped in hot pitch at the same temperature. He also mentions the use of linseed oil as an addition to the pitch to keep it of the right consistency, and give a tough elastic coating.

Undoubtedly the finest material for this method of protection is natural asphaltum or bitumen, to which enough heavy mineral oil has been added to give a tough and elastic film. Pitch from petroleum ('maltha') has much the same characters. The Sabin process consists in dipping in a hot coating mixture like the above, draining, and then heating for two hours in a vertical oven at 400° F. Steel water mains up to 5 feet diameter, and in sections weighing 5 tons, have been treated by this process in America, and the United States Navy adopted the process for copper fire mains and flush mains, which are rapidly acted upon by salt water. It has also been employed for the small steel tubing for electric conduits which require an elastic and tough coating.

Heavy coal tar is commonly employed for hot dipping of cast-iron pipes. In practice the process amounts to distillation of the more volatile portions of the tar from the hot pipe, leaving a pitch coating, so that success is largely dependent on the correct dipping temperature. The soft pitch obtainable from tar produced in the low temperature distillation of coal will undoubtedly prove one of the best commercial products in this country. Tar acids and ammonia compounds are both undesirable constituents of tar for this purpose, as both tend to increase corrosion.

The anti-corrosive or protective paints are widely applicable. They may be classified as :—

1. Linseed oil paints, containing some drier, and usually also a proportion of varnish.

2. True varnish paints (enamels) consisting mainly of resins and oil.

3. Varnishes made from a natural resin with a volatile solvent. Each of the above will carry pigment, of which a large proportion is usually iron oxide (Fe_3O_4).

4. Asphalts, or coal-tar pitch, with a certain amount of boiled linseed oil, dissolved in a volatile solvent, such as coal-tar naphtha or petroleum naphtha.

In general, whilst the linseed oil paints are cheaper and easy to apply, they are not so satisfactory as the varnish paints, in which the natural gum or resin reduces the porosity of the film. This has been particularly noticed in the case of coatings for plates submerged in water. Also the more elastic the kind of varnish the better the result. Class 3 constitutes an important class of protective compositions specially suited to ship use, where the slow drying ordinary type of varnish can seldom be employed owing to lack of time for drying. The volatile spirit rapidly evaporates, leaving the resin and oil binding the pigment.

Cushman and others, from the results on steel plates in water carrying various pigments in suspension, obtained a classification of these ingredients of paints into 'inhibitors,' 'indeterminates,' and 'stimulators.' (Proc. Amer. Soc. for Testing Materials, Vols. III. to VIII., 1903-1908.) The result is, in part, dependent on the purity of the pigment, but, broadly, zinc pigments, chrome green, Dutch process white lead, and some Prussian blues fall in the 'inhibitor' class; lamp black, other carbon blacks, precipitated barium sulphate (blanc fixe), ochre and bright red oxide, and some Prussian blues are 'stimulators.' Such a classification would appear to have little value if the pigment particles are thoroughly 'sealed' in the paint medium, but if through porosity, or absorption of water, electrical contact between the pigment particles and the iron is established, the activity of the pigments is probably of the order given; the results certainly suggest an advantage of a first coating with one of the inhibitor class.

The most perfect protection with paints is afforded by enamels (varnish paints or 'japans') which have been stoved on to the metal; a good example is seen in cycle frames, &c. The stoving treatment causes the resin and oil to flow into a perfect film, free from porosity, and to set with a fine hard surface. The one objection is the liability to chip with a blow. For under-water work stoved metal is said to show little advantage, and Sabin states that unbaked varnish paints are better.

Coating with another metal less liable to corrosion includes zinc galvanising and tin plating, both of which are carried out by hot dipping the thoroughly cleaned plate in the molten metal. For more special work electro-deposition of copper or nickel (usually on a first coating of copper), and of other metals is occasionally employed. Electro-deposition of zinc is also largely employed for certain classes of work, such as frames, &c., for ships.

These deposits afford a fair protection, but even with the best class of nickel plating, as applied to cycle parts, rusting under wet conditions is found to occur. Should the metal protecting film become broken, so exposing the iron beneath, in most cases this exposure leads to more rapid rusting, as the iron is electro-positive to the protecting metal, and galvanic action at its expense is set up. Zinc coatings are, however, free from this defect, and as long as a good surface of zinc is still in contact with the iron, it will be the former metal which is mainly attacked. Tin plate offers a complete contrast in this respect.

A special process for applying zinc is the sherardising process of Cowper Coles. The cleaned articles are packed in metal vessels with zinc dust, a mixture of finely divided zinc and zinc oxide, and heated for several hours at a temperature below the melting-point of zinc. This metal slowly penetrates the iron, and to a far greater depth than with hot galvanising ; a hard alloy is formed which is practically non-corrodible, and is capable of being polished.

Processes dependent upon the formation of a protective skin date from the old Bower-Barff process, where the heated iron was treated with steam, so that a film of the black oxide (Fe_3O_4) was formed. The good surface of 'Russian iron' is due to a similar film, and as long as the film remains intact, protection is excellent, but rusting is accelerated once the film is broken. A more recent process is that of Coslett, in which the iron is immersed in a dilute solution of phosphoric acid. Later the inclusion of a subsequent dipping in chromic acid was patented by Coslett. Richard and Adams have patented a process in which the article is immersed for from 2 to 20 minutes in a solution made by dissolving 1¼ lbs. of manganous carbonate in boiling phosphoric acid (60 fluid ounces of B.P. phosphoric acid to 87 fluid ounces of water).

Another process aims at the production of a

film of nitride of iron, the article being heated in a suitable gaseous mixture, such as ammonia, or treating the highly heated metal in a bath of salts which will yield gases capable of forming the nitride.

Protection by 'inhibiting' the corrosive action almost invariably involves dipping in dilute chromic acid.

One of the most successful methods of preventing corrosion, especially in the case of boilers and condensers, is that of Elliott Cumberland. The galvanic action leading to corrosion is overcome by inserting insulated iron anodes, these being connected to the positive pole of a small dynamo ; current always passes from the anode to the part to be protected, which forms the cathode. A difference of potential of 6–10 volts is usually employed. In the case of brass tube condensers 1 ampere per 500 square feet of surface is found to ensure complete protection. In the case of boilers it is found that the hydrogen set free at the cathode plates or tubes is very effective in preventing the formation of a hard scale.

Corrosion of Boilers.—A serious form of corrosion is to be found in the rusting and pitting of the plates and tubes of high-pressure boilers. Before the adoption of mineral lubricants, it was supposed that the decomposition of the lubricating oils by the superheated steam in the cylinders caused the corrosion owing to the fatty acids liberated, but the same effect has been found with hydrocarbon oils, so that the pitting is evidently not due to this cause.

There are several causes which lead to the corrosion found in boilers, amongst which are ordinary corrosion, set up by the carbon dioxide and oxygen which occur naturally in all water, and which act on the metal when the boiler is out of use. This form of corrosion can be prevented by filling the boiler quite full with boiled water rendered slightly alkaline with a little lime and closing air-tight whilst at rest. The most frequent cause of corrosion in land boilers is dissolved salts, or free acids and alkalis in the feed water, which become concentrated solutions by evaporation. Acid waters, notably those collected in peaty districts, are particularly injurious Nitrates and nitrites, chloride and nitrate of magnesia are salts most liable to cause corrosion. Complete analyses of the saline constituents of the water can alone determine the requisite treatment required to prevent corrosive action. Secondly, galvanic action, induced by the difference in potential between the rust formed by ordinary corrosion and the iron, and also by metallic impurities in the iron and specks of foreign metals deposited upon it. This action can be prevented to a great extent by the use of zinc blocks inside the boiler and in metallic connection with the iron of the plates, or by the Cumberland system already described. A third cause of corrosion is to be found in the solvent action of distilled water upon the metal of the boiler, the action getting less with increase in the quantity of salts in solution in the water. The fourth cause arises from high local temperatures, often not far below a dull red heat, and then iron decomposes water, forming black magnetic oxide of iron and liberating hydrogen :

$$4H_2O + 3Fe = Fe_3O_4 + 4H_2$$
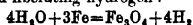
Overheating is most likely to be due to deposits or incrustations, and in such cases is checked, or stopped, by the sole use of condensed water, or a properly softened natural water, for the feed.   J. S. S. B.

CORROSION AND FOULING OF STEEL AND IRON SHIPS. AND ITS PREVENTION. In the days of wooden ships the hull troubles that had to be guarded against were the attacks of wood-boring animals and the loss of speed due to the growth of weed and shell at and below the water line ; but with the launch of the first sea-going vessel built of iron, in 1822, comparatively simple problems became of great complexity, and at the present time the protection of our Navy and mercantile marine from corrosion and fouling is a question of the greatest importance, affecting, as it does, both the life and speed of the vessels.

Corrosion.—The troubles due to corrosion are by no means limited to the exterior plates of the ship, but also affect the interior of the structure, boilers, and condensers.

The corrosion of iron and steel is brought about by the actions which ultimately result in the conversion of the metal into oxides, and these being accelerated by galvanic actions, which it is almost impossible to eliminate in a huge metallic structure like the hull of a modern ship in the presence of sea water, makes prevention far more difficult than in the case of an iron building or bridge.

In sea water the process of corrosion is accelerated by the salts contained therein, as these aid the galvanic action set up in the metal by various means, such as impurities in the iron, the presence of mill scale on the plates, high temperature, or even the different stresses imparted to portions of the same plate, whilst in certain waters, such as the mouths of rivers on the west coast of Africa, or in harbours where the water contains much sewage, the sulphates are decomposed by various vegetable and animal organisms with evolution of sulphuretted hydrogen, which greatly increases the corrosion of the metal.

The examination of the condition of the bottom plates of vessels that have been at sea for long periods, shows. when the protective paints and compositions have been removed, that three distinct forms of rusting may be distinguished.

1. Rust patches, generally near the edges of the plates, consisting of small areas of fine rust, probably caused by moisture on the plate when the protective paint was on. These patches are never thick, and cause but little damage to the plates if all rust be removed before a new coating of paint is put on.

2. Rust nodules are a more localised form of corrosion which has attacked the metal where particles of mill scale have been left on the surface of the new plate, or where small particles of slag or foreign matter have been rolled into the plate during manufacture. These give slight pitting of the plate, but seldom to a serious extent.

3. Rust cones are an accentuated form of rust nodules, and are due to the most local form of galvanic action, caused by the presence of a speck of deposited copper, lead, or other foreign metal, or even a small particle of rust

or mill scale left on the surface of the iron, and covered by the compositions used as protectives and antifoulers. As soon as the sea water penetrates these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister; the hydrogen escapes and water leaks in, the action becoming more and more rapid, and the blister gradually filling with the product of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being easily distinguished in a well-formed cone, and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

Certain portions of a ship's hull are exposed to special risk of corrosion from galvanic action, owing to the bearings of the screw shaft and valves for the escape of waste water, bilge, &c , being made of alloys containing copper. In order to prevent this, zinc protectors, consisting of heavy masses of the metal, are placed round all openings where copper or copper alloys are present, and the zinc, being more electro-positive than the iron, places the iron in the electro-negative condition, so that whilst the iron escapes injury the zinc rapidly dissolves. The Cumberland process (*vide supra*) has been successfully employed in such cases, insulated iron anodes being fixed to the hull close to the part to which it is necessary to afford protection.

The general procedure for protecting the exterior of the bottoms of iron and steel ships from corrosion is to coat them with so-called anti-corrosive or protective paints and varnishes. In order that this should be successful, much depends upon the state of the hull at the time at which the protective is put on.

The bottom plates of the newly built vessel are thickly coated, as a rule, with mill scale or magnetic oxide of iron Fe_3O_4, which is formed on the surface of the plate during rolling, and which, if it remains perfectly intact, would be an excellent protective, as it forms, indeed, the basis of the Bower-Barff process for the protection of iron; but during the shearing and riveting of the plates this scale gets broken off and exists only in patches, which, if left upon the plate, would excite rapid local galvanic action, owing to the fact that this scale is strongly electro-negative to the iron, so that it would need only the exciting influence of the sea water to start the action.

In naval vessels, the plates are pickled in dilute sulphuric acid, as already described, until all the scale is removed. In the mercantile marine it is an ordinary practice to launch a vessel without any paint on the hull, leaving the active, but fairly even, rusting which ensues to remove the scale, the ship being scrubbed down and then protective compositions painted on when it is docked.

This method has the advantage of cheapness, and also of giving a very slightly roughened surface, to which the protective composition adheres firmly, and answers well with tramp steamers and other craft where speed is not an object of paramount importance; but with service vessels and liners, slight as the roughening is, it undoubtedly has an influence on the speed.

The hull of the vessel, being perfectly free from mill scale, and as free as it can possibly be got from the ordinary oxide, is then painted with the protective, but for this to prove effective, the hull must be absolutely dry, a condition which it is exceedingly difficult to obtain, as the big mass of iron is generally a few degrees in temperature below that of the moisture-laden air, and under these conditions a trace of moisture condenses on the surface, which is spoken of as 'sweating' of the metal, and this prevents the proper adhesion of the paint to the metallic surface, and also starts rusting under the paint.

Oil paints are the oldest form of protectives in use, and, when the plates are painted when hot and dry, amongst the best and most lasting ; but the drying of such paints, being dependent upon the slow oxidation of the boiled oil by air into a resin, requires that a considerable time must elapse between the painting of the ship and the coating becoming hard enough to allow of the anti-fouling composition being painted on over it, and as a rule so short a time is allowed for docking that this is a great drawback.

The old paints for this class of work used to consist of red or white lead mixed with boiled linseed oil, but it was shown by M. Jouvin that with the perishing of the vehicle the lead compounds were converted into chlorides and oxychlorides by the sea water, and these were then reduced by the action of the iron of the hull with formation of crystals of lead, which set up galvanic action and led to rapid corrosion.

Spirit varnish protectives came into use when it became necessary to cut down the time expended in docking, and they owe their rapid drying powers to the fact that, instead of waiting for oxidation to form a resinous mass, as in the drying of boiled oil, a resin is dissolved in a highly volatile solvent, being mixed with boiled linseed oil to give the necessary elasticity, and when this is painted on the hull of the vessel, the rapid evaporation of the solvent leaves the resin and oxidised oil binding the body colour together.

Shellac, rosin, kauri, and many other gums and resins are used, whilst the solvents may consist of light hydrocarbons, such as the various grades of solvent naphtha, alcohol, and even fusel oil, but in the Navy very low flash-point solvents have now been discarded owing to the danger in storage.

The drawbacks to the last two classes of protectives are that the solvents employed for dissolving resins and gums are mostly affected by water, with the result that if the plates are not dry, the resins are apt to be deposited in a pulverulent condition, whilst the cold produced by the rapid evaporation of the solvent tends to increase the amount of moisture deposited, which assists in the deterioration of the coating. Alcohol varnishes have, however, the great advantage that they are not so affected by moisture on the metal, or deposited moisture, since the spirit will absorb a moderate amount of water.

These varnishes also, even when dry, are not impervious to gases and liquids. Under a microscope the coating is seen to be full of minute pores, through which the sea water finds its

way to the iron beneath, and, when once corrosion has been started, the protective coating is gradually forced away from the surface of the iron, exposing more metal to be acted upon. The best results are secured by employing several coats of the varnish, and applying it only in weather favourable to the operation, plenty of time being given for the thorough hardening of the material before water comes in contact with it.

In most of the various paints red oxide of iron is used to give body and colour to the mixture, and, as it is the same colour as the rust that may form under it, it is very popular with the composition manufacturer, and, providing it be free from acid and soluble sulphates, is unobjectionable ; but perhaps a better material would be the mixture of finely divided zinc and zinc oxide, such as is obtained in the Belgian process of distilling zinc, as, even after the varnish had perished, the zinc would afford a further term of protection. After extensive trials the U.S Naval Authorities adopted an anti-corrosive paint of the following composition : gum shellac, 7·9 lbs ; turpentine, 0 6 gallon ; pine oil, 0 6 gallon ; alcohol, 7¼ gallons ; dry metallic zinc, 9½ lbs. , white zinc oxide, 28½ lbs. ; the above making 10 gallons.

The protection of the interior surface of the hold of a ship presents some special complexities, as it is exposed to the wear and tear of taking in and discharging cargo and one has to take into consideration such sources of trouble as the action of bilge water, the high temperature, and the presence of foreign bodies such as coal-dust and leakages from cargo There are three classes of protectives used for the interior portion of a ship :

Cements ;

Bituminous coatings ;

Paints.

Although cement is very largely used, yet there are certain drawbacks attached to it which render it by no means the ideal material It has a certain amount of porosity, so that any corrosive liquid penetrates it and acts on the iron beneath ; its rigidity causes it to come away from the metal on any strain being thrown on the latter, variations in temperature having the same effect, and where the coating has parted from the iron, corrosion will start and remain unseen until perhaps too late.

Bituminous coatings applied hot are far preferable to cement, but are rather more troublesome to put on.

Fouling of ships and its prevention. The question of the fouling of ships' bottoms is one that has existed from the earliest days, and was of even more importance formerly than it is at the present time, owing to the increase in dock accommodation allowing the more frequent cleaning and painting of the ships ; but even now in the case of war the loss in speed during blockading operations, owing to the fouling of the vessels, might prove an important factor in a struggle for supremacy.

Fouling consists of various marine growths, both animal and vegetable, which attach themselves to the bottom of the vessel, and by increasing the skin friction whilst the vessel is in motion, seriously reduce its speed.

The nature of these growths needs to be studied in properly equipped marine biological laboratories, as but little is at present known of the life-history of many of the organisms which are found on a ship's bottom. The main factors, however, are that it is only during the germ or spore period of their existence that they can attach themselves to the bottom of the vessel, and that although the full-grown results are found when the vessel is docked, these growths have taken place *in situ*.

The open ocean and the northern seas are comparatively free from these organisms, but directly inland seas or tropical waters are reached they increase to an enormous extent in variety and numbers, and some harbours, such as the port of Sourabaya, are noted for the fouling influence of their waters. Moreover, it is found that the period of the year exercises a very important influence upon the fouling nature of the water, the spring and early summer being the chief time for these growths to find a lodgment on the bottom of a vessel.

The more common growths are serpulæ, generally called coralline, barnacles, mussels, membranæ, and oysters, usually classified together under the name of ' shell,' whilst at or near the water line are found luxuriant growths of sea grass (*Enteromorpha compressa* and *Zostera marina*), and towards the bottom ribbon and other weeds, like the tufted weed or bugula, flourish

Fouling commences with the deposition of a slight slime on the side of the vessel, which is apparently of an albuminous nature, and contains the germs and spores of various marine growths, and is so slight as to escape notice.

The first visible sign of fouling on a ship is the appearance of green grass at the water line, and this, in bad waters, will begin to show after a few weeks, whilst the growth will spread downwards from the surface for 5 or 6 feet, but rarely extends below 10 feet, as the growth needs plenty of light and warmth.

It is the most widely distributed form of fouling, and appears in nearly all waters, and, once formed, the grass protects the germs of other growths, and so helps on the general fouling.

In northern waters fouling seldom goes beyond the ' grass,' but in warm climates, especially if long in port, ' shell ' soon begins to appear, unless a really good anti-fouling composition is employed for coating the vessel's bottom.

Ships trading to or stationed near the mouths of rivers often show curious results in the kind and extent of the fouling, the marine growths being often killed by the fresh water, but such vessels foul again very rapidly when once more going to sea, owing to slight deposits of mud and calcium carbonate from the river water.

With wooden ships the necessity of protection against the wood-boring teredo worm as well as fouling led to the adoption of copper sheathing, and when the metal used was of a fairly pure character, it was found to be thoroughly satisfactory, and not only to give complete protection to the vessel, but also to enable it to remain at sea for a very considerable period. The cost, however, was high, and attempts were made to prevent the excessive waste of the copper by using zinc protectors, as advocated by Sir Humphry Davy, but it was soon found

that with the prolongation of the life of the copper plates, fouling again became serious, whilst when later rolled sheets of alloys containing zinc, such as Muntz metal, were tried, the same trouble again appeared, and it has been clearly proved that the power a copper plate exercises in preventing fouling is inversely proportional to its power of resisting the action of the sea water.

The action of the copper in anti-fouling is that, in the first place, the salts in solution in the sea water act upon the copper with the formation of chlorides and oxychlorides, the former poisonous to all forms of marine life in the germ state, whilst the latter formed a coherent pellicle to which the growths attached themselves and which was torn off during the passage of the vessel through the water by the skin friction, thus enabling it to shed any form of growth that might have attached itself to the plate by a process of scaling.

It was found, however, that if the copper were not of the purest, coralline growths very soon attached themselves so firmly through the surface of the skin of copper compounds that it was difficult to remove, and gave points of adherence for fresh vegetable growths.

With the introduction of steel and iron ships, as was natural, attempts were made to utilise the same form of protection from fouling which had proved so satisfactory with wooden ships, and from time to time during the past efforts have been directed to sheathing iron ships with copper in the same way. It was soon found, however, that this sheathing set up such severe galvanic action with the hull of the vessel as to be impracticable, and although these attempts were abandoned at a very early period in the mercantile marine, the naval services of several countries have tried its use for service vessels, the generally adopted method being to sheathe the iron hull with wood and to attach to this the copper in such a way as to be insulated from the electro-positive iron, but if water penetrated the insulation was broken down. The alternative of saturating dry wood with paraffin wax has been suggested.

With increase in dock accommodation, the tendency has been more and more towards the use of anti-fouling paints or compositions, which could be painted on over the protective coating of the vessel, and a number of compositions have been placed on the market with varying success for this purpose.

When anti-fouling paints were first manufactured, the only fact at the service of the maker was the experience which had been gleaned from copper sheathing, and on the assumption that the action had been due to the poisonous character of the chloride and oxychloride of copper produced on the plates by the salts in the sea water, compositions were made containing large quantities of corrosive metallic poisons, which, held in a varnish of a more or less lasting character, gave the protection from fouling for a few months

As has already been pointed out, the action of the copper sheathing was due to two causes : first, the poisonous action of the copper salts on the germ life ; and, secondly, the stripping of the pellicle by skin friction when any quantity of growth had formed on its surface, an action

termed 'exfoliation.' How important this latter action was may be judged from the fact that when the vessel remained at anchor in a harbour, the sheathing would last from 10 to 12 years, whilst when on active service the same sheathing would last for only 4 or 5.

Finding that poisons alone gave very unsatisfactory results, the manufacturers of anti-fouling compositions began to make perishable varnishes and grease paints, which should, by the deterioration and wasting of their surface, imitate as nearly as possible the exfoliation of the copper sheathing, and such anti-foulers gave under certain circumstances much more successful results. The idea was that the ship, having been coated with a protective paint or composition to preserve the iron, a second or more coatings was put on over the protective, consisting of varnish paints which should slowly yield soluble poisons to the sea water, and in doing so would lead to the disintegration of the varnish surface, which, being washed off, exposed fresh quantities of the poisons to the water.

Such compositions proved very satisfactory in the mercantile marine, and all the time that a vessel was actively engaged in going from port to port gave excellent results, but directly these same compositions, which had gained a reputation in the merchant service, were tried on Service vessels, they were found to be as unsatisfactory as those which before had been in use. The reason for this failure is evident. Take the case of a liner trading between New York and England : she is run at a high speed between these two ports for the main portion of her life, remaining in the basin for as short a period as possible in order to utilise to the full her money-earning capacity ; for such work it is easy to arrange an anti-fouling composition, which, with the aid of the skin friction of the vessel, would cause just sufficient wasting of the coating to give the best results. When, however, this is applied to a Service vessel, she probably goes out from dock into the basin and remains there stationary for perhaps months, and then goes to sea, where she is kept manœuvring at various rates of speed for a considerable period. During the period she is in the basin, the composition undergoes practically no wasting, and a thin film of carbonate of lime and mud deposits on the surface, which forms an excellent foothold for any germs and spores that may be in the water, and which, on going to sea, have often advanced too far for the growth to be readily got rid of.

The bad results so obtained led to a composition being put on which wasted with sufficient rapidity to prevent any such deposition in harbour, with the result that when the vessel went to sea, the deterioration being accelerated to an enormous extent by skin friction, the composition was practically all exhausted in a very short time.

The most efficient anti-fouling compositions all contain copper or mercury as the poison. In some cases soluble salts of these metals are employed with a fairly strong and lasting varnish ; in others oxides or insoluble salts are used with varnishes which perish more rapidly on their surfaces and allow the action of the

sea water to convert the compounds into soluble salts.

It is evident that with compositions containing such metallic compounds every attention must be paid to the protection of the hull, as otherwise the formation of soluble salts of copper and mercury might result in the deposition on the iron of these metals by reduction, in which case rapid galvanic action would be set up, and would lead to serious pitting of the plates of the vessel.

The compositions of the present day may be divided into two classes :

1. Grease paints containing a metallic poison ;
2. Quick-drying varnish paints, also charged with the same poisonous constituents.

The former class has met with a considerable degree of success, but they have also several very serious drawbacks As regards the prevention of fouling, they give results not very far-removed from the best varnish paints, and in certain waters, such as the Mediterranean, have proved themselves to be excellent antifoulers, but they undoubtedly increase the skin friction of the vessel, and so tend to diminish speed ; whilst a second trouble is that, although a varnish paint may often be scrubbed and touched up where fouling has been but slight, with a grease paint the whole has to be removed before recoating, and they are much more costly than the varnish paints, with the result that in the merchant service they are used only to a very limited extent. Another drawback to their use is that it is impossible to properly scrape and recoat the vessel during the short period of docking which would suffice for a varnish paint.

In the manufacture of varnish paints it is necessary to mix with the solution of gum or resin in a volatile solvent a sufficient proportion of linseed oil to give elasticity to the vehicle, and these paints have been in use in England since about 1870, the greatest advance in them being due to the introduction of the hot process in their manufacture, which enables a more intimate mixture to be made with greater adhesive power and a smoother surface.

The rate at which disintegration of these paints takes place is governed largely by the kind of gum used in the varnish, and by the amount of mineral matter introduced as colouring and poisonous material, the solubility of these having a considerable influence on the rate of disintegration.

With a tough and tenacious vehicle, which by itself would undergo but little disintegration under the action of sea water, it is quite possible to use soluble mercury or copper salts, which are liberated only very slowly during the gradual destruction of the varnish. On the other hand, if a rosin varnish be employed, insoluble bodies, like the oxides of copper and mercury, the subchloride of mercury, or Scheele's green (copper arsenite), may be used, the oxides and other salts, when exposed to the sea water, being very slowly converted into soluble chlorides.

Many compositions contain arsenic and arsenic compounds, such as sodium arsenite, as these had been found effective as weed killers under ordinary conditions, and it was expected that in a composition they would prevent the growth of grass at the water line, which, as it caught the eye, gave the impression of the ship being very foul. Experience showed, however, that the arsenic had but little effect, and mercury and copper still remain pre-eminently the metallic poisons of the greatest value in anti-foulers. H. Williams, Naval Constructor, U.S. Navy, has given the following composition for a paint adopted with great success for naval vessels : grain alcohol, 6 gallons ; gum shellac, 13¼ lbs. ; turpentine, 1 gallon ; pine-tar oil, 1 gallon ; white zinc oxide, 13¾ lbs. ; Indian red, 13¼ lbs. ; red oxide of mercury, 4¼ lbs. It was found that the cost of this paint was only one-third of the price charged for the proprietary paints.

In some anti-fouling varnish paints the poisonous metals themselves have been carried in a very fine state of division, some paints containing very finely divided copper, precipitated from the solution of a copper salt by iron or zinc , whilst others contain metallic mercury in a comminuted condition, obtained by adding stannous chloride to the solution of a mercurous salt ; these paints, however, show but little advantage over those containing salts of the metals.

One of the most difficult portions of the ship to deal with is what is known as the ' boot top,' that is, the portion between the heavy and light load line, as when a ship is discharging cargo the anti-fouling composition over this portion is exposed to the sun and rapidly perishes and peels off, whilst when the ship is again loaded, it is once more immersed, and the alternate action of sunshine and air and sea water perishes the paint at the very spot where it is most likely to be abraded by contact with lighters and barges, the result being that it is often necessary to touch up this portion of the vessel with paint during the voyage, and as good anti-fouling paints are rarely carried for this purpose, this portion of the ship is often painted with ordinary paint, and hence is liable to more damage than other parts of the vessel.

V. B. L.

CORROSIVE SUBLIMATE (*Mercuric chloride*) *v.* MERCURY.

CORUBIN *v.* ABRASIVES.

CORUNDUM. (*Corundon*, Fr. ; *Korund*, Ger. ; from the Sanskrit name *korund*.) Crystallised alumina (Al_2O_3). The crystals belong to the rhombohedral system, and are isomorphous with hæmatite (Fe_2O_3). They vary considerably in habit, having the form of hexagonal prisms, pyramids, or tables. In some crystals the combination of six faces of the primary rhombohedron with two faces of the basal plane produces a form strikingly similar to the regular octahedron. There is no true cleavage, but often the crystals and crystalline masses show a pseudo-cleavage or parting parallel to the basal plane or to one or more faces of the primary rhombohedron, due to lamellar twinning on these planes. On these surfaces the lustre is sometimes pearly, but otherwise it is usually vitreous, or inclining to adamantine in character. The fracture is uneven to conchoidal ; and the sharp jagged edges of the irregular grains give effect to the cutting power of the material when used as an abrading agent. Analyses show the presence of 95-99 p.c. of alumina, with small

amounts of ferric oxide, magnesia, silica, water, &c., and sometimes traces of chromium. Sp.gr. 3·9–4·1. The crystals are optically uniaxial and negative; refractive indices for sodium light $\omega=1·7690$, $\epsilon=1·7598$. The dichroism is marked. Next to diamond, it is the hardest of minerals, being placed as No. 9 in the scale of hardness; on this account it was formerly known as adamantine spar.

A distinction is made between the transparent 'precious corundum' and the dull, opaque 'common corundum,' while a third still less pure variety is known as emery (q.v.). This division also corresponds with the economic uses of the mineral, 'precious corundum' being used for gem-stones, and 'common corundum' and emery for abrasive purposes. The pure, well-crystallised material is perfectly colourless and transparent with a high degree of brilliancy. Traces of inorganic impurities, however, produce a wide range of colours, which are more vivid in the stones of gem-quality, namely red (ruby), orange and yellow ('oriental topaz'), green ('oriental emerald'), blue and indigo (sapphire), and violet ('oriental amethyst'). Parti-coloured stones are not uncommon. The colour of common corundum is usually grey or brown.

Corundum is not a widely distributed mineral, but it is found in abundance at certain localities. It occurs in igneous and metamorphic rocks, such as granite, syenite, gneiss, peridotite, and serpentine, and in crystalline limestones. Material of gem-quality is usually collected as water-worn pebbles in gravels derived from these rocks. Material for gem-stones and for abrasive purposes is not, as a rule, mined in the same localities. Taking first the localities for the gem-varieties, the following may be noted as a few of the most important. The best rubies are obtained from the famous mines near Mogok in Upper Burma, where they occur in a white crystalline marble near its contact with gneiss; they are mined in this rock and also in its products of decomposition. Dark-coloured rubies are obtained with sapphire from alluvial deposits in the provinces of Chantabun and Krat in Siam. Stones of good quality have also been mined together with common corundum in Macon Co., North Carolina. The best sapphires come from the gem-gravels of Ceylon; other localities of importance are Siam and Kashmir. Dark-blue and greenish-blue sapphires occur abundantly in gravels near Anakie in Queensland; while paler stones of various shades ('fancy stones') are plentiful in the neighbourhood of Helena in Montana.

Common corundum as used for abrasive purposes (apart from emery, q.v.) was formerly mainly mined in the United States; later the Canadian deposits came into prominence; while now the latter are being ousted by the artificial products carborundum and alundum. India has also since remote times produced a certain amount which has been largely used by the native lapidaries. In the United States the corundum deposits extend along the Appalachian Range from Alabama to Massachusetts, reaching their greatest development in North Carolina and Georgia. Here they occur in peridotites near their contact with gneiss. In Canada a belt of corundum-bearing syenites

(nepheline and related alkaline syenites), associated with the Laurentian gneisses, extends for 100 miles across Renfrew, Hastings, and Haliburton counties in Ontario, the principal mining district being near Craigmont in Renfrew Co. Large rough crystals of corundum are abundant in gneiss in Madagascar and at Steinkopf in Namaqualand, South Africa. More recently, important deposits have been discovered and worked in the Zoutpansberg and Pietersburg districts in northern Transvaal.

The corundum-bearing rock as mined is crushed between hardened steel rolls and the heavier corundum separated in water by means of jigs and concentrating tables. It is sifted into different grades of fineness and used (1) as loose grains; (2) mixed with glue or other soft cement as a coating on paper or cloth; and (3) as corundum-wheels for grinding. The last named are of three classes: (a) The 'vitrified wheel,' in which the corundum is mixed with clay and baked at a high temperature, with the result that the grains of corundum are set in a matrix of porcelain. (b) The 'chemical wheel,' in which sodium silicate is the binding material. (c) The 'cement wheel' with shellac, rubber, linseed-oil, &c., or magnesium oxychloride. Another use for corundum, depending on its hardness, is for the pivot supports for watches (watch-jewels) and other delicate instruments, the poorer qualities of gem-material being used for this purpose. Although corundum is the richest ore of aluminium, there are difficulties in its use for the extraction of the metal. It has, however, been used directly in the preparation of aluminium-copper and aluminium-iron alloys.

The artificial preparation of crystallised corundum was first effected by M. A. Gaudin, in 1837, by decomposing potash-alum with charcoal. It has since then been produced by a variety of methods, and is now manufactured on a large scale both for use as gem-stones and for abrasive purposes. Beautiful crystals of ruby were prepared by E. Frémy and Feil, in 1877, by heating a mixture of alumina and red-lead with potassium dichromate in a porous fireclay crucible; a fusible aluminate of lead was thereby formed, which was decomposed by the silica of the crucible with the separation of crystallised alumina. The crystals so obtained, though of some size, good colour, and perfectly transparent, were unfortunately too thin for cutting as gems. A far greater measure of success was achieved by A. Verneuil in 1902, who has produced fine gems of all colours (v. GEMS, ARTIFICIAL). Interesting experiments from a petrological point of view were conducted by J. Morozewicz in 1898, in which he obtained crystallised corundum in silicate magmas supersaturated with alumina. Artificial corundum, used as an abrasive under the trade name of alundum (aloxite, adamite), is now manufactured on a large scale at Niagara Falls by fusing bauxite in an electric furnace. 'Corubin' is also an artificial corundum, formed as a by-product in the Goldschmidt thermite process.

References.—A. E. Barlow, Corundum, its Occurrence, Distribution, Exploitation, and Uses, Canada, Dept. Mines, Geol. Survey, Mem. 57, Ottawa, 1915, 378 pp. (with special reference to the Canadian deposits); T. H. Holland,

Corundum, Manual of the Geology of India, 2nd edit., Calcutta, 1898 (with special reference to the Indian deposits) ; G. P. Merrill, The Non-metallic Minerals, 2nd edit., New York, 1910 ; J. H. Pratt, Bull. U.S. Geol. Survey, 1906, No. 269 ; J. H. Pratt and J. V. Lewis, North Carolina Geol. Survey, 1905, i. ; P. A. Wagner, South African Journ. Industries, 1918, i, 776 ; Trans. Geol. Soc. S. Africa, 1919, xxi 37 ; M. Bauer, Edelsteinkunde, 2nd edit., Leipzig, 1909, and English translation by L. J. Spencer, London, 1904 ; Sapphire-Mining Industry of Anakie, Queensland, Bull. Imp. Inst., London, 1916, xiv. 253.   L. J. S.

CORYBULINE, CORYCAVINE v. CORYDA-LINE.

CORYDALINE AND THE CORYDALIS ALKALOIDS. These alkaloids occur in the roots of the *Corydalis tuberosa* (DC) (syn *C cava, C. bulbosa, Bulbocapnos cavus*), belonging to the Fumariaceæ, and also in some other species of this genus (*C. ambigua, C. vernyi, C nobilis*). Corydaline was discovered by Wacken-roder, in the year 1826 ; and forty years later Wicke (Annalen, 1866, 137, 274) described the alkaloid more fully, assigning to it the formula $C_{18}H_{19}O_4N$. An investigation by Adermann (Inaug. Dissert., Dorpat, 1890) indicated that *C. cava* contained three or four different alka-loids, and the formula $C_{20}H_{23}O_4N$ was attributed to the one which is now regarded as corydaline

This base was more completely examined by Dobbie and Lauder (Chem. Soc. Trans. 1892, 61, 244, 605), and Josephi (Annalen, 1893, 277, 1), who respectively ascribed to it the formula $C_{22}H_{24}O_4N$ and $C_{22}H_{27}O_4N$, the latter being probably the more correct formula. About the same time Freund and Josephi isolated three other alkaloids from *C. cava* roots, namely *bulbocapnine, corycavine*, and *corybulbine* ; whilst Dobbie and Lauder described a fifth, *corytuberine* (l c 1893, 63, 485).

Several other corydalis alkaloids have since been isolated, the chief of which are *dehydro-corydaline, isocorybulbine, corycavamine, cory-cavidine,* and *corydine*. Gadamer, Ziegenbein, and Wagner have classified the principal alka-loids into the following three groups :—

	Corydaline	$C_{22}H_{27}O_4N$
(1)	Dehydrocorydaline	$C_{22}H_{23}O_4N$
	Corybulbine	$C_{21}H_{25}O_4N$
	*iso*Corybulbine	$C_{21}H_{25}O_4N$
	Corycavine	$C_{23}H_{25}O_6N$
(2)	Corycavamine	$C_{21}H_{21}O_5N$
	Corycavidine	$C_{22}H_{25}O_5N$
	Bulbocapnine	$C_{19}H_{19}O_4N$
(3)	Corytuberine	$C_{19}H_{21}O_4N$
	Corydine	$C_{20}H_{23}O_4N$
	*iso*Corydine	$C_{20}H_{23}O_4N$

The alkaloids in the first group are of weakly basic character, those in the third are strong bases, and the members of the second group are intermediate in this respect. All are oxidised by iodine, the first group yielding berberine-like compounds, except in the case of dehydro-corydaline, which is, itself, already such a com-pound. The third group will contain phenolic hydroxyl, and are therefore dissolved by alkalis.

Protopine and two other alkaloids, one of which has the formula $C_{20}H_{17}O_4N$, and is isomeric with berberine, have been found in

Chinese corydalis tubers (*C. ambigua*), as well as the first three members of Group 1 (Makoshi, Arch. Pharm. 1908, 246, 381). Five more alkaloids, including *glaucine*, have been obtained from parts of *C. tuberosa* by Haars and by Gadamer (Arch. Pharm. 1905, 243, 154 ; and 1911, 249, 224).

To separate the chief corydalis alkaloids Gadamer, Ziegenbein, and Wagner extract the ground root with alcohol, distil off the solvent, dilute and acidify the residue with acetic acid. After filtering, the acid filtrate is purified by extraction with ether, then made ammoniacal, and the alkaloids extracted by means of ether. From the ethereal solution, after most of the solvent has been distilled off, a mixture of corydaline, bulbocapnine, corycavine, and cory-bulbine is deposited ; these are separated, in the order given, by successive extractions with boiling alcohol. More corydaline is obtained from the mother liquor on further concentration. The residue evaporated to dryness is converted into hydrobromides and fractionally precipi-tated with ammonia, this treatment giving more corydaline, and also corybulbine, *iso*corybulbine, corycavamine, corycavine, corydine, and bulbo-capnine, in the order named. Corytuberine remains in the ammoniacal solution, and is obtained by extraction with chloroform after evaporating the solution to a syrupy consistency. To purify the crude corydaline it is converted into the hydrochloride and precipitated, together with some corycavine, from an aqueous solution by addition of alkali ; any bulbocapnine present remains in solution, and can be recovered by passing carbon dioxide into the alkaline liquid. The corydaline and corycavine may then be separated by repeated crystallisation from absolute alcohol ; corydaline, being the more soluble of the two, accumulates in the later fractions.

Corydalis roots have been used in pharmacy, and are credited with antiperiodic properties. The alkaloids have a narcotic effect, but are not employed in medicine. The members of the three groups above-mentioned are closely related in physiological action as well as chemical constitution. According to Peters (Arch. expt. Path. Pharm. 1904, 51, 130) and Gadamer (Arch. Pharm. 1905, 243, 147), the alkaloids of the corydaline group produce paralysis of the spinal cord, and those of the corycavine group stimulate the motor centres ; whilst the members of the bulbocapnine group give rise to increased reflex action. All except corytuberine induce in frogs narcosis like that due to morphine, and have a prejudicial effect upon the action of the heart. It has been suggested that bulbocapnine may be useful as a narcotic in veterinary prac-tice, in the case of animals on which morphine has a stimulating effect.

Group 1. *Corydaline* $C_{22}H_{27}O_4N$ crystallises from alcohol in hexagonal prisms, m.p. 134·5°, $[\alpha]_D^{20} +317°$ in chloroform or $+310°$ in alcohol. It dissolves easily in ether, chloroform, carbon disulphide, benzene, or warm alcohol, but is sparingly soluble in cold alcohol, and insoluble in water or alkalis. Corydaline and its solutions are quickly coloured yellow by the action of light or heat. It gives well-crystallised salts. The *aurichloride* ($B·HCl)_2AuCl_3$ crystallises from

dilute alcoholic hydrochloric acid as orange-coloured needles, m.p. 207° ; the *platinichloride* (B·HCl)$_2$PtCl$_4$ forms brown crystals, m.p. 227° ; the *hydrochloride* B·HCl,2H$_2$O, columnar crystals, m.p. 206°–207° ; and the *ethyl sulphate* B·C$_2$H$_5$HSO$_4$H$_2$O, large colourless prisms, m.p. 152·5°.

On oxidation with iodine in alcohol corydaline yields *dehydrocorydaline*, which occurs with it in *Corydalis tuberosa* (Schmidt, Arch. Pharm. 1908, 246, 575). Four methoxyl groups are present in corydaline, and the base contains a tertiary nitrogen atom, since it reacts with methyl iodide to form corydaline methiodide B·CH$_3$I. Oxidised with permanganate, it gives eventually hemipinic and *meta*-hemipinic acids, showing the presence of two benzene nuclei in the molecule At the same time, another oxidation product, *corydaldine* C$_{11}$H$_{13}$O$_3$N, is formed ; and from the constitution of this the presence of an *iso*quinoline nucleus in the original alkaloid is inferred.

On oxidation of corydaline with dilute nitric acid instead of permanganate, dehydrocorydaline is first produced. One of the benzene nuclei is next destroyed, and a yellow dibasic acid, *corydic acid* C$_{16}$H$_{17}$O$_6$N + $\frac{1}{2}$H$_2$O, is formed When corydic acid is in turn oxidised with permanganate, it yields first an insoluble, colourless, tribasic acid C$_{17}$H$_{15}$O$_8$N, *corydilic acid*, and eventually *meta*hemipinic acid, and a methyl pyridine tricarboxylic acid, which latter on further oxidation is converted into pyridine-2 : 3 : 4 : 6-tetracarboxylic acid C$_9$H$_5$O$_8$N. The position of the methyl group in the tricarboxylic acid is thus indicated ; and from this and the foregoing results the following constitutional formulæ for corydaline and dehydrocorydaline are deduced (Dobbie and Lauder, Chem. Soc. Trans 1892, 61, 605 ; 1894, 65, 57 ; 1897, 71, 657 ; 1899, 75, 670 ; and 1902, 81, 145) :—

Corydaline.   Dehydrocorydaline.
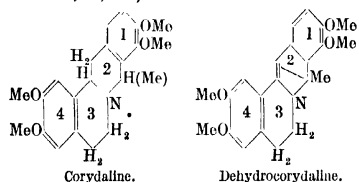
This formulation indicates the close relationship shown by these alkaloids with tetrahydroberberine and berberine respectively. The former differs from corydaline only in having a dioxymethylene group substituted for the two methoxyl groups in ring 4, and a hydrogen atom for the methyl group in ring 2. Between the absorption spectra of corydaline and tetrahydroberberine there is also a very close relation ; in fact, the only difference is that the general absorption shown by tetrahydroberberine is slightly greater than that of corydaline (Chem. Soc. Trans. 1903, 83, 598).

By reduction of dehydrocorydaline two optically inactive corydalines are produced, *r*-corydaline, m.p. 135°, and *r*-mesocorydaline, m.p. 158°–159°, the two compounds being stereoisomeric. The former is obtained when an aqueous solution of dehydrocorydaline hydro-chloride is treated with platinised zinc and dilute sulphuric acid at the temperature of the water-bath. Its sulphonic acid can readily be resolved by means of brucine into the corresponding *l*- and *d*-salts. *r*-Mesocorydaline is obtained together with its isomeride under milder conditions of reduction, by keeping an alcoholic solution of dehydrocorydaline hydrochloride with zinc-dust and sulphuric acid at the ordinary temperature until it is decolourised. The separation of the two bases is easily effected by crystallisation from ether, the *r*-mesocorydaline alone separating (Gadamer and Klee, Arch. Pharm. 1916, 254, 295). By means of the camphorsulphonate it can be resolved into active components, but neither the *l*-form nor the *d*-form is identical with natural corydaline.

Dehydrocorydaline C$_{22}$H$_{23}$O$_4$N occurs in the roots of *C. tuberosa*, *C. ambigua*, *C. solida*, and *C. vernyi*. From corydaline it is produced by the action of mild oxidising agents, such as dilute nitric acid. It is a yellow crystalline powder, m.p. 112°–113° (deomp.), and gives crystalline salts ; the aurichloride B·HAuCl$_4$ forms red-brown needles, m.p. 219°. It gives a crystalline oxime, m p. 165° : and, like berberine, unites with one molecule of chloroform, yielding a colourless crystalline compound, m.p. 154°. Haars ascribes the formula C$_{22}$H$_{25}$O$_5$N to dehydrocorydaline, and regards the alkaloid as having a keto-structure when in the free state, but as being a quaternary base when in solution (Arch Pharm. 1905, 243, 165).

Corybulbine was first separated by Freund and Josephi (*l c.*) from commercial corydaline, and more fully investigated by Dobbie and Lauder, who assigned to it the formula C$_{21}$H$_{25}$O$_4$N (Chem. Soc. Trans. 1894, 65, 25). It is soluble in boiling alcohol, from which it separates, on cooling, as a fine crystalline powder, m.p. 238°–240°. It is practically insoluble in water, sparingly soluble in ether and in methyl alcohol, readily in carbon disulphide, chloroform, and hot benzene. The solution in chloroform is dextrorotatory, $[a]_D^{20} + 303\cdot3°$. Corybulbine gives well-crystallised salts ; the *hydrochloride* B·HCl forms yellowish prisms, m.p. 245°–250°. On oxidation with iodine in alcohol corybulbine gives *dehydrocorybulbine* C$_{21}$H$_{21}$O$_4$N, m.p. 210°–211°, and on treatment with hydriodic acid furnishes 3 molecules of methyl iodide. On methylation with methyl iodide in the presence of potassium hydroxide, it yields corydaline, so that it differs from the latter only in containing an —OH group in place of an —OMe group, probably in the *iso*quinoline nucleus (Dobbie, Lauder, and Paliatseas, Chem. Soc. Trans. 1901, 79, 87).

iso-*Corybulbine* C$_{21}$H$_{25}$O$_4$N, first obtained by Gadamer, Ziegenbein, and Wagner, and subsequently examined by Bruns (Arch. Pharm. 1902, 240, 19), crystallises from alcohol in voluminous leaflets, m.p. 179°–180°, $[a]_D + 299\cdot8°$ in chloroform, and, on oxidation with iodine in alcohol yields *dehydroisocorybulbine*

$$C_{21}H_{21}O_4N$$

The latter resembles dehydrocorydaline and dehydrocorybulbine, and its hydriodide reduced with zinc and sulphuric acid gives *i*-iso*corybulbine*, m.p. 165°–167°. Three methoxyl groups

are present in *isocorybulbine* (*cf.* Bruns, *idem.* 1903, 241, 634).

Group 2. *Corycavine* $C_{23}H_{23}O_4N$ was first obtained by Freund and Josephi (Annalen, 1893, 277, 15). It is insoluble in water and in alkalis, sparingly soluble in cold, but more readily in hot absolute alcohol, from which it crystallises in rhombic tablets, m.p. 218°-219°; the alkaloid is optically inactive. The *hydrochloride* $B·HCl,H_2O$ forms broad needles, m p 219°; the *hydriodide* $B·HI,H_2O$ has m.p 236°; and the *aurichloride* $B·HAuCl_4$ has m p. 178°-179° (decomp). With methyl iodide it reacts as a tertiary base, the methiodide produced forming rhombic tablets, m p. 218°. Corycavine contains a dioxymethylene group, but no —OH or —OMe group (Ziegenbein, Arch. Pharm. 1896, 234, 523; and Gaebel, *idem.* 1910, 248, 207).

Corycavamine $C_{21}H_{21}O_4N$, like corycavine, contains no methoxyl group, but probably a dioxymethylene group. It is a crystalline base, forming rhombic columns, m.p. 149°, and has $[a]_D^{20}+166·6°$ in chloroform; but on heating at 180°, or by warming with acetic anhydride, it may be converted into an optically inactive modification, m p. 213°-214°, resembling cryptopine (Gadamer, Ziegenbein, and Wagner, Arch. Pharm. 1902, 240, 81)

Corycavidine $C_{22}H_{25}O_5N$ has been described by Gadamer (*idem* 1911, 249, 30). The mixed amorphous alkaloids of *C. cava* on conversion into thiocyanates can be separated into two groups, one giving crystalline thiocyanates, soluble with difficulty in alcohol, the other readily soluble, and amorphous From the second group corycavidine was isolated It is crystalline, and has m.p. 212°-213°, $[a]_D^{20}+203·1°$ in chloroform. It appears to be corycavamine, in which a dioxymethylene group is replaced by two methyoxyl groups. Like corycavamine, it is converted on heating into the optically inactive form, m.p 193°-195° after recrystallisation ; the change occurs at 209°. Corycavidine crystallises from hot chloroform with 1CHCl₃ on addition of alcohol. It forms a crystalline hydrochloride and nitrate. The aurichloride $BHAuCl_4$ is a red powder, which sinters at 85° and melts at 170° (decomp.).

Group 3. *Bulbocapmine* $C_{19}H_{19}O_4N$ was obtained by Freund and Josephi from the roots of *Corydalis cava* (Annalen, 1893, 277, 10). It separates from hot absolute alcohol in rhombic needles, m.p. 199°, $[a]_D+237·1°$ in chloroform, and yields crystalline salts. The *hydrochloride* $B·HCl$ forms needles, m.p. about 270°; the *hydrobromide* $B·HBr$ has m.p. 250°-270°; the *hydriodide* $B·HI$, m.p. 230°-270°; and the *platinichloride*, m p. 200°-230° (decomp.). The *methiodide* $B·CH_3I$ forms shining needles, m.p. 257°.

Bulbocapnine is insoluble in water, but dissolves in alkalis, and is precipitated from its solutions in these by addition of carbon dioxide or ammonium chloride. Its four oxygen atoms are accounted for by the presence of a methoxyl, a hydroxyl, and a dioxymethylene group (Gadamer and Kuntze, Arch. Pharm. 1911, 249, 503, 598). Further, ' exhaustive methylation ' gives rise to 3 : 4-dimethoxy-5 : 6-dioxy-methylene-8-vinyl-phenanthrene, which brings

bulbocapnine into close relationship with apo-morphine. The same authors have investigated the other members of this group, and assign the following formulæ to the four alkaloids concerned (*ibid.* 641) :—

Bulbocapnine.

Corytuberine.

Corydine.
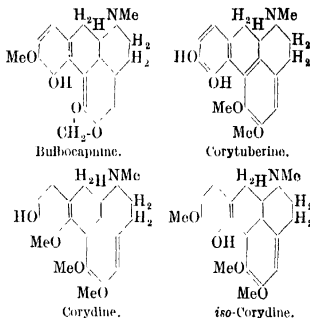
iso-Corydine.

Corytuberine $C_{19}H_{21}O_4N,5H_2O$ was obtained by Dobbie and Lauder from commercial cory-daline by extraction with hot water (Chem. Soc. Trans. 1893, 63, 485) It crystallises from alcohol in fine, silky needles, m.p. 240°, $[a]_D^{20}+282·6°$ in alcohol. The alkaloid is nearly insoluble in cold water, ether, or chloroform, slightly soluble in benzene, and dissolves readily in hot water or in solutions of alkalis. It forms crystalline salts, including a methiodide. Two methoxyl and two hydroxyl groups are present. On methylation with methyl sulphate or diazo-methane a mixture of two isomeric monomethyl ethers is obtained ; these correspond with corydine and *iso*corydine The dimethyl ether of corytuberine is glaucine. Corytuberine in alkaline solution is readily oxidised by air, giving a dark green liquid Its physiological action is very similar to that of apomorphine ; and as with bulbocapnine and corydine, the characteristic emetic effect disappears when the two hydroxyl groups are methylated (Gadamer, Arch. Pharm. 1902, 240, 81 ;, and 1911, 249, 503, 641).

Corydine $C_{20}H_{23}O_4N$ was first described by Merck, and later by Gadamer and his collaborators (*idem.* 1902, 240, 81 ; 1911, 249, 669). It crystallises from alcohol with ½EtOH, m.p 124°-125°, or 149° dry ; $[a]_D^{20}+204·3°$ in chloroform. Three methoxyl groups and one hydroxyl group are present in the alkaloid. Oxidised with iodine, it yields the hydriodide of dehydro-corydine $C_{20}H_{19}O_4N·HI$, which, on reduction, gives *i*-corydine, m.p. 165°-167°. From this *l* corydine is obtained by recrystallisation of the *d*-tartrate. As shown above, corydine is a monomethyl ether of corytuberine.

iso*Corydine* $C_{20}H_{23}O_4N$ is obtained, as already shown, by methylating corytuberine. It crystallises in tablets, m.p. 185°, and has $[a]_D^{20}+195·3°$ in chloroform. Its *methiodide* has m.p. 213°-214°, and $[a]_D^{20}+143·3°$.

J. J. D.

CORYFIN. Trade name for ethyl glycollic

menthyl ester $C_{10}H_{19}O\cdot CO\cdot CH_2\cdot O\cdot C_2H_5$ used in the treatment of nasal catarrh.

COSMOS REDS *v.* AZO- COLOURING MATTERS.

COTARNINE *v.* OPIUM.

COTO BARK. True coto bark is obtained from Bolivia, the Amazons (Brazil), and Venezuela. It has been considered identical with Winter's bark [from *Drimys Winteri* (Forst.)], but its source is really unknown (Jobst and Hesse, Annalen, 282, 191). It comes into the market in long strips about 8 cm. broad and 12 mm. thick, and is tough and hard. The colour is cinnamon brown, and a cross section shows numerous yellow spots. It has an aromatic odour, and contains *cotoin*, *dicotoin*, *hydrocotoin* and *methyl-hydrocotoin*, resins, tannin, &c. The supply of the true coto bark is limited, so inferior barks, chiefly *para-coto bark*, are sold. These contain little or no cotoin, but instead *protocotoin* and *methyl-protocotoin*.

Cotoïn or *Benzoyl-phloroglucinol-mono-methyl ether* $C_{14}H_{12}O_4$, is found, together with various

OH

OH
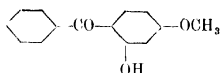
related substances, in true coto bark, but not in para coto bark, and has been the subject of much investigation by Ciamician and Silber (Ber. 24, 299 and 2977; 25, 1119, 26, 777; 27, 409 and 841; 28, 1549), Jobst (N Repert Pharm. 1876, xxv. 23; Ber. 11, 1031), Jobst and Hesse (Ber 10, 249; Annalen, 199, 17), and Hesse (Ber. 26, 2790; 27, 1182; Annalen, 282, 191). As a result its constitution has been made clear and a number of its derivatives described.

Cotoïn can be isolated from true coto bark by extracting the powdered bark with cold ether, distilling off the ether from the extract, and mixing the residue, whilst still hot, with light petroleum, whereupon a resinous-oily mass separates, from which the solution of cotoïn can be decanted and the product obtained from it in the form of large yellow crystals. A further quantity can be obtained from the resinous mass mentioned above by boiling it with lime-water, and treating the solution obtained with hydrochloric acid, when the cotoïn is precipitated. Cotoïn may be recrystallised from alcohol, or hot water, when it separates in yellow prisms, melting-point 130°-131°C. It is difficultly soluble in cold water, readily soluble in hot, is fairly soluble in alcohol, ether, and chloroform, but sparingly soluble in light petroleum or benzene. It dissolves in alkalis forming yellow solutions from which it is reprecipitated on acidification. As decomposition products of cotoïn, phloroglucinol as also benzoic acid have been obtained.

Cotoïn has been used pharmaceutically in cases of diarrhœa and of phthisis.

The *diacetyl derivative* $C_{18}H_{16}O_6$, produced by the action of acetic anhydride, or acetic anhydride and sodium acetate, on cotoïn, consists of large prisms, melting-point 94° C. If sodium acetate is used in the acetylation, the diacetyl derivative is accompanied by the

acetyl derivative of *methoxy-hydroxy-phenyl-coumarin acetate*, melting-point 142°C.—
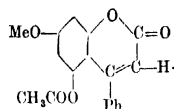
Benzoyl cotoïn, obtained by the action of benzoyl chloride on cotoïn, crystallises in prisms, melting-point 110°-112°C.

Dibenzoyl-cotoïn consists of needles, melting-point 134°-135°C.

Dimethyl-cotoïn, obtained by the action of methyl iodide and alkali on cotoïn, crystallises from alcohol, and has melting-point 138° C. It yields a mono-acetyl derivative, colourless needles, melting-point 150° C., hence the formula

$$HO\cdot C_6H\cdot Me(OMe)_2\cdot CO\cdot C_6H_5$$
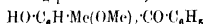
has been proposed for it by Ciamician and Silber.

Dibromcotoïn $C_{14}H_{10}O_4Br_2$, which crystallises in large colourless needles, melting-point 116° C., is prepared by the action of bromine on cotoïn in chloroform solution.

Cotoïn oxime $C_{14}H_{13}NO_4$ crystallises in plates, soluble in alcohol, difficultly soluble in water, and has been prepared by the action of hydroxylamine hydrochloride on a cold aqueous solution of cotoïn in sodium carbonate.

Mono-nitroso-cotoïn consists of dark red leaflets, or orange-yellow needles (from acetic acid), melting-point 153°-154° C (both forms). The needle variety possibly contains acetic acid of crystallisation (Pollak, Monatsh. 1901, 22, 996).

A dilute solution of cotoïn in sodium carbonate is capable of coupling with diazonium compounds, and in this way Perkin and Martin (Chem. Soc. Trans. 1897, 1149) have prepared the following derivatives :—

Cotoïn-azo-benzene $C_{14}H_{11}O_4\cdot C_6H_5N_2$ crystallises from acetic acid in orange-yellow needles, melting-point 183°-184° C. ; it yields a *diacetyl* derivative, $C_{14}H_9O_4\cdot(C_2H_3O)_2\cdot C_6H_5N_2$, when treated with acetic anhydride and sodium acetate, scarlet needles, melting-point 155°-156° C. ; on treatment with hot alkalis the acetyl compound is hydrolysed with formation of the free azo compound.

Cotoïn-azo-o-toluene, similarly prepared from diazotised *o*-toluidine and cotoïn, orange-yellow needles, melting-point 203°-204°C.

Cotoïn-azo-p-toluene consists of orange-yellow needles, melting-point 207°-208°C.

Hydro-cotoïn, which occurs together with cotoïn, is a *dimethyl ether of trihydroxy-benzoyl-benzene*, $C_6H_5\cdot CO\cdot C_6H_2(OH)(OMe)_2$.

A number of poly-hydroxy benzophenone derivatives, including products found in coto bark and related to cotoïn, have been prepared by W. H. Perkin and Robinson (Proc. Chem. Soc., 1906, 305).   A. G. P.

COTTON consists of the long hairs which cover the seeds of various species of *Gossypium*, a genus of the nat. ord. *Malvaceæ.* The botanical classification of cotton is in a confused state, and this is doubtless mainly due to the cultivation of the plant for extensive periods, the large

interchange of seed which has taken place between the different countries of production, and the consequent gradual modification of the distinctive characters of the original species.

American cottons.—The ordinary Upland cotton is fairly generally considered to be derived from *Gossypium hirsutum* (Linn.). Some authorities, however, are of opinion that it is derived from *G. herbaceum* (Linn.), whilst others regard these two species as identical. Sea Island cotton has usually been regarded as *G. barbadense*, but is considered by Watt (Wild and Cultivated Cotton Plants of the World) to be a hybrid form.

Egyptian cottons.—The Egyptian cottons probably cannot be referred to any particular species, but are mostly hybrid forms of *G. barbadense* with other species. Most commonly, Egyptian cottons are regarded as *G. barbadense*, but Watt places them under *G. peruvianum* (Cav.), which some authorities consider as identical with the former

Indian cottons —With reference to these varieties, G. A. Gammie, of the College of Science, Poona, writes, in his monograph on The Indian Cottons : ' It is clearly evident that we have at the most only one true species of cotton in India, *Gossypium obtusifolium*, with its two sub-species, *G. arboreum* and *G. herbaceum* All other forms should be treated as derivatives of these.' Other botanists, however, regard the Indian cottons as derived from various distinct species, including *G. herbaceum, G. neglectum, G. Wightianum,* and *G. arboreum.*

Brazilian and Peruvian cottons – Brazilian cotton is generally considered to be the product of *G. brasiliense* (Macf.), and rough Peruvian cotton that of *G. peruvianum* (Cav)

The cotton plant grows as a shrub or small tree. It is of perennial habit, but, in cultivation, is usually treated as an annual. In certain districts of Brazil and Peru, however, arborescent forms are grown, which are allowed to remain in the ground for several years. When the flower-bud first opens, the petals are generally white or pale yellow, but they gradually become darker and redder until the third or fourth day, and then fall to the ground. The young fruit remains attached to the flower-stalk and enveloped in the calyx ; it gradually increases in size, and is known as the ' boll.' When the boll is ripe, it dehisces by from three to five valves, exposing the cotton, which, now that the pressure on it is released, rapidly expands and forms a large fluffy mass. As soon as the boll has opened completely, and is quite dry, the cotton is ready to be gathered. The seeds, with the cotton fibre adhering to them, form the product known as ' seed cotton ' ; this is collected from the ripe bolls, and the cotton (or ' lint '), after being torn from the seeds by the process of ' ginning,' constitutes the raw cotton of commerce. Seed cotton usually consists of about one-third of its weight of cotton fibre and two-thirds of seeds.

The cotton fibre is composed of a single hollow cell, and, while unripe, has the form of a long narrow tube. As the fibre matures, it becomes more or less flattened, and presents the appearance of a narrow, somewhat opaque ribbon or band, with slightly thickened, rounded edges. The ripe fibre possesses a peculiar characteristic twist. This twist appears to be an acquired character ; it is not present in wild cotton, and is increased by care in cultivation. The number of twists in a given length is very variable, and, as a rule, is, roughly speaking, inversely proportional to the diameter of the fibre, the twist being most numerous in the finest variety (Sea Island). Unripe cotton consists of thin, transparent fibres with little or no twist. Such fibres are known technically as ' dead cotton,' and, being very weak and brittle, they break up in the process of manufacture, thus increasing the amount of waste, and also tending to weaken the yarn or fabric into the composition of which they enter ; they also possess the defect of not being able to take dyes satisfactorily.

According to the length of the individual fibres, cottons are classed in commerce as long-, medium-, or short-stapled. The long-stapled cottons are 1¼ inches or more in length, the medium-stapled are about 1 inch long, and the short-stapled are less than 1 inch. The principal long-stapled varieties are Sea Island cotton, Egyptian varieties, and the improved American Upland forms, which have been evolved from the ordinary Upland kinds by continuous selection and careful cultivation. The Brazilian and Peruvian cottons vary from about 1 to 1½ inches, and are, therefore, either medium- or long-stapled. The chief medium-stapled cottons are the ordinary American Upland kinds, and the short-stapled class is represented by the Indian varieties.

Sea Island cotton is grown in South Carolina, Georgia, Florida, and the West Indies. The fibre is very long, fine, silky, and of a lustrous creamy tint, and this cotton is therefore the most valuable variety. It is used in commerce for spinning the finest and best yarns. Considerable care is required in the cultivation of this cotton, and the yield per acre is usually lower than that of other kinds.

American Upland cottons are produced in enormous quantities in the United States, and are the principal kinds used in the Lancashire spinning industry. They are of longer staple and better quality than the Indian varieties, and are employed for the manufacture of yarns of medium quality.

Egyptian cottons exist in several varieties, most of which yield a fibre of a brownish tint. These cottons are long, strong, and fine, and more lustrous than American Upland, but inferior to Sea Island cotton. Egyptian cotton is preferable to American Upland for the manufacture of goods requiring a soft, smooth finish and high lustre.

The Indian cottons are mostly short and coarse, and are consequently less valuable than American Upland kinds. The chief markets for these varieties are Japan and Germany, comparatively little being imported into the United Kingdom.

Brazilian cotton is harsh and wiry, of medium strength and of good length. One of the varieties grown in North Brazil is a tree cotton, which lives for 8 years or more. The ordinary annual cottons are more largely cultivated and are more productive than the arborescent form, but the fibre of the latter has the longer staple.

Peruvian cotton is chiefly of two kinds,

known respectively as 'rough' and 'smooth.' The former is the product of a cotton tree which is allowed to remain in the ground for from 4 to 6 years; the fibre is well known for its peculiarly harsh and crinkly character, which renders it especially useful to spinners for mixing with wool. 'Smooth' Peruvian is very similar to American Upland cotton, and is used for the same purposes.

The following table gives the approximate length and average diameter of the fibres of the principal commercial varieties. The diameters of the fibres of any one variety show great variation among themselves, but the figures given under this head are the average of a large number of determinations by various observers, and can, at least, be regarded as relatively accurate :—

Variety		Usual length	Average diameter
		inches	inch
Sea Island	.	1·6–2·2	0 00064
American Upland	.	0 8–1 1	0·00077
Egyptian .	.	1·3–1·6	0 00068
Indian .	.	0 6–1 0	0·00084
Brazilian .	.	1·1–1·4	0 00080
Peruvian (rough)	.	1·2–1·5	0·00078
„ (smooth)	.	0·9–1·1	0·00077

Cotton consists of about 83 7 p.c. of cellulose (q.v.), together with 7 p.c. of water, 0 6 p.c. of wax and oil, 1·5 p c of protein, and about 1·65 p.c of mineral matter (ash) (Bull. 33, U.S. Dept. Agric). The actual composition of cotton varies with its origin

The wax is present as a thin layer on the surface of the fibre, and renders it incapable of absorbing water readily. This substance, to which Schunck (Manchester, Mem. Lit. Phil. Soc. [iii.] 4, 95) has given the name 'cotton wax,' resembles other vegetable waxes, such as cerosin prepared from the leaves of the sugar-cane, and the waxes from the leaves of the carnauba palm [*Copernicia cerifera* (Mart.)], and the raphia palm [*Raphia pedunculata* (Beauv.). It is insoluble in water, but soluble in alcohol or ether; it melts at 86°, and solidifies again at 80°–82°. Pure cotton wax is insoluble in solutions of caustic alkali; it contains C 80 4, H 14 5, O 5 1. Associated with this wax is a fatty acid, which was regarded by Schunck as margaric acid, but is more probably a mixture of stearic and palmitic acids; it melts at 55·5°, and resolidifies at 50·5°.

The oil in the cotton fibre appears to be identical with that contained in the seed. In the preparation of the so-called absorbent cotton wool, the wax and oil are removed by boiling the fibre with dilute caustic alkali under pressure; the material is subsequently washed, treated with bleaching powder and hydrochloric acid, again washed, and dried.

The nitrogenous constituents of cotton consist of the remains of the cell protoplasm and allied substances.

The mineral substances contained in the fibre are chiefly phosphates, chlorides, and sulphates of potassium, sodium, magnesium, and calcium, together with small quantities of iron

and traces of aluminium. If the amount of ash is much more than 2–3 p.c., the excess is probably due to the presence of sand and other mechanical impurities.

When cotton is immersed in a strong solution of caustic soda, it undergoes certain remarkable changes, the chief of which is the production of a silky lustre. This phenomenon was discovered by John Mercer in 1844, and has led to results of great commercial importance. The process is now carried out on an extensive scale under the name of 'mercerisation' (q.v.), and is sometimes applied to the yarn and sometimes to the woven fabric. The material is either kept in a state of tension during the operation, or is allowed to shrink in the alkaline liquid, and afterwards stretched to its original length before being washed The process not only produces an exceedingly high lustre on the cotton, but also increases its power of absorbing dyes. The structure of the cotton fibre undergoes alteration; the flattened, twisted tube, characteristic of ordinary cotton, swells out, and is thus converted into a hollow, cylindrical form. This change is accompanied by a decrease in length and also by an increase in tensile strength, mercerised cotton being in some cases as much as 50 p.c. stronger than ordinary cotton. Egyptian cotton generally mercerises better than ordinary American cotton.

When cotton is treated with a mixture of nitric and sulphuric acids, it is converted into nitro-cellulose or gun-cotton (v. EXPLOSIVES). On dissolving gun-cotton in ether, or a mixture of ether and alcohol, the product known as collodion is obtained (v. PHOTOGRAPHY). Nitro-cellulose also enters into the composition of celluloid (q.v).

Among the more important works on this subject may be mentioned The Cotton Plant, Bull No 33, Office of Expt. Stat. U.S. Dept. of Agric.; Bowman's Structure of the Cotton Fibre; and Oppel's Die Baumwolle.   E. G.

**COTTON BROWNS, SCARLETS, YELLOWS,** *v.* AZO- COLOURING MATTERS; PRIMULINE.

COTTON FLOWERS. Among the various portions of the cotton plant which have been industrially employed must be included the flowers which constitute one of the numerous Indian dyestuffs. According to Watt (Dictionary of the Economic Products of India) they are thus used in the Manipur district. *Gossypetin* was first isolated in small quantity from the flowers of the ordinary Indian cotton plant, *G. herbaceum* (Perkin, Chem. Soc. Trans. 1899, 75, 826), and has been more completely studied at a later period (*ibid.* 1913, 103, 650). For its preparation a concentrated alcoholic extract of the flowers is treated with hot water and the mixture digested when boiling with addition of hydrochloric acid for three hours. After removal of tar by filtration the hot liquid on cooling deposits a brownish-yellow powder, which contains a mixture of quercetin and gossypetin. These colouring matters are separated by a fractional crystallisation of their mixed acetyl derivatives from acetic anhydride, acetylgossypetin being in these circumstances the least soluble. The acetyl compound is finally hydrolysed by sulphuric acid in the presence of acetic acid in the ordinary manner.

Gossypetin $C_{15}H_{10}O_8$ forms yellow needles,

melting-point 311°–313°, closely resembles quercetin in appearance, and is readily soluble in alcohol, but only very sparingly soluble in water. Concentrated alkaline solutions dissolve it, forming orange-red liquids which on agitation and dilution with water, become green, then blue, and finally assume a dull brown tint. Alcoholic lead acetate gives a deep red precipitate in the cold, passing into dull brown at the boiling-point, and with alcoholic ferric chloride a dull olive-green liquid is obtained.

Gossypetin like quercetin forms compounds with mineral acids which crystallise in orange-red needles, and with alcoholic potassium acetate the *monopotassium* derivative $C_{15}H_9O_8K$ is produced. The *hexa-acetyl* derivative

$$C_{15}H_4O_8(C_2H_3O)_6$$

forms colourless needles, melting at 228°–230°. By fusion with alkali or by dissolving the colouring matter in cold 50 p.c. aqueous potassium hydroxide and allowing the solution to remain exposed to air for twenty-four hours, with shaking, *protocatechuic acid* is obtained. A phenolic substance also produced by these methods of hydrolysis has not yet been identified.

When methylated with excess of methylic iodide and methyl alcoholic potash *gossypetin hexamethyl ether* $C_{15}H_4O_2(OMe)_6$, colourless needles, melting-point 170°–172°, is produced, and this by hydrolysis with alcoholic potash gives *protocatechuic acid dimethyl ether* and *gossypitol tetramethyl ether* $C_{12}H_{16}O_6$, needles, melting-point 115°–116°. By ethylation in a similar manner, *gossypetin hexaethyl ether* $C_{15}H_4O_2(OEt)_6$, melting-point 144°–146°, can be prepared, and with alcoholic potash yields *diethylprotocatechuic acid* and *gossypitol tetraethyl ether* $C_{16}H_{24}O_6$, melting-point 110°–111°. The latter forms an *oxime* $C_{16}H_{25}O_6N$, melting-point 127°–129°, and when oxidised with permanganate gives *gossypetonic acid*, yellow needles, melting-point 154°–155°. The constitutions assigned both to this latter (1) and to gossypitol tetraethyl ether (2) are given below:—

(1) $HO \cdot C_6H(OEt)_3CO \cdot CO_2H$

(2) $HO \cdot C_6H(OEt)_3CO \cdot CH_2 \cdot OEt$

and from these that of gossypetin naturally follows:—

When an alkaline solution of gossypetin is exposed to air the blue liquid on acidification yields a reddish-brown precipitate which on gentle warming becomes crystalline. Again, if benzoquinone is added to a solution of gossypetin in cold absolute alcohol a similar reaction takes place. On keeping for a few minutes crystals commence to separate, and by then heating to 50° a semi-solid mass is obtained.

Gossypitone $C_{15}H_8O_8$, the name assigned to this substance, consists of microscopic needles of a dull red colour, which are difficultly soluble in the usual solvents. It dissolves in dilute alkalis with a pure blue colouration and its solution in concentrated sulphuric acid is dull brown. Sodium hydrogen sulphite solution reconverts it into gossypetin. Gossypitone possesses strong

dyeing properties, and gives the following shades on mordanted woollen cloth:—

Chromium.	Aluminium.	Tin.
Dull brown.	Orange-brown.	Orange-red.
	Iron.	
	Deep olive.	

These, it is interesting to note, are identical with those given in these circumstances by gossypetin itself, and it is accordingly evident that during the dyeing operation oxidation of the latter to gossypitone takes place. Until a definite knowledge of the tetrahydroxybenzene nucleus in gossypetin has been obtained the position of the hydroxyl groups in this portion of the molecule can only be conjectured. Existing as it does side by side with quercetin it seems natural to consider that gossypetin is a hydroxyquercetin. Again, should gossypitone be a *p*-quinone, the constitution of gossypetin will be the same as that which Neirenstein and Wheldale have suggested (Ber. 1911, 48. 3487) for the flavonol (1) which they obtained from quercetone, an oxidation product of quercetin, but the descriptions of the two compounds are not in agreement [1] On the assumption of the necessity for a quinol nucleus in gossypetin a second constitution (2) is however possible.—

Again, a third expression (3), representing gossypetin as an hydroxyquercetin, is available, though in this case gossypitone must be regarded as an ortho- rather than a para-quinone:

The glucosides present in cotton flowers have been examined by Perkin (Chem. Soc. Trans. 1909, 95, 2181), who in the first place employed the Egyptian variety. The Egyptian cottons appear, according to the researches of Messrs. Fletcher and Balls, to be derived from natural crosses of brown Peruvian cottons with the Sea Island variety.

A concentrated alcoholic extract of the flowers deposits on cooling a semi-crystalline powder, and this consists mainly of the potassium salts of two glucosides, quercimeritrin and gossypitrin, whereas a third glucoside iso-quercitrin is present in the filtrate. A rough separation of the latter from this mixture may also be effected by means of aqueous lead acetate, for in these circumstances the precipitation of isoquercetin does

[1] This compound, more recently synthesised by Neirenstein (Chem. Soc. Trans. 1915, 107, 872), is described as melting at 354°–355°, and its hexamethyl ether at 145°–147°.

not occur, at least to any extent. The isolation of quercimeritrin and especially of gossypitrin in a pure condition from these flowers is however of too tedious a character to be described here, and for details of the processes involved the original paper must be consulted.

Quercimeritrin $C_{21}H_{20}O_{12}$, $3H_2O$, melting-point 247°–249°, consists of small, glistening, bright yellow plates, insoluble in cold and fairly readily soluble in boiling water. Its alkaline solutions possess a deep yellow tint; with aqueous lead acetate it gives a bright red precipitate, and with ferric chloride an olive-green colouration. *Octa-acetylquercimeritrin*, needles, $C_{21}H_{12}O_{10}(C_2H_3O)_8$, melting-point 214°–216°, is sparingly soluble in alcohol, whereas *monopotassium quercimeritrin*, a yellow powder, can be obtained by means of alcoholic potassium acetate. By hydrolysis with dilute sulphuric acid quercimeritrin yields quercetin and glucose according to the following equation :—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$
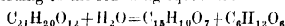
and is thus analogous to quercitrin which in this manner is converted into quercetin and rhamnose.

On wool mordanted with aluminium, tin, chromium, and iron, quercimeritrin gives the following shades :—

Aluminium.	*Tin*	*Chromium*
Orange-yellow.	Bright orange.	Reddish-brown
		Iron
		Olive-brown.

And these results are interesting, because with the exception of the iron mordanted pattern, which is of a rather browner character, the colours thus produced closely resemble those which are given by quercetin itself when dyed in a similar manner. They are widely different from those given by rutin and quercitrin, and mainly as a result of this property there can be little doubt that quercimeritrin is to be represented by one of the two following formulæ :—

$$C_6H_7(OH)_4 \cdot O \left\langle \begin{array}{c} O \\ \\ OH \end{array} \right. \begin{array}{c} C--- \\ \parallel \\ CO \end{array} C \cdot OH \left\langle \begin{array}{c} OH \\ \\ \end{array} \right\rangle OH$$

$$HO \left\langle \begin{array}{c} O \\ \\ \end{array} \right. \begin{array}{c} C--- \\ \parallel \\ CO \end{array} C \cdot OH \left\langle \begin{array}{c} OH \\ \\ \end{array} \right\rangle OH$$

$$C_6H_7(OH)_4 \cdot O$$
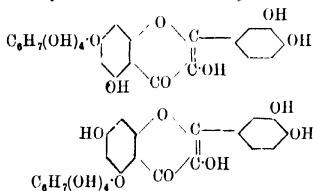
Quercimeritrin is also present in the flowers of the *Prunus emarginata* ? (Finnemore, Pharm J. 1910, (iv.), 31, 604).

Gossypitrin $C_{21}H_{20}O_{13}$, only isolated with considerable difficulty. is more readily prepared from the *G. neglectum* (see below). When crystallised from dilute acetic acid it contains $2H_2O$ of crystallisation, and is readily dissolved by hot water, but on boiling this solution yellow needles of the anhydrous substance, melting-point 240°–242°, separate. When anhydrous it does not absorb water of crystallisation from moist air, but on boiling with acetone the hair-like needles are broken up into much finer needles, which when dried at 100° possess 1 molecule of water of crystallisation. Such a preparation melts at 200°–202°, and when dried

at 160° on standing in air now absorbs water. Preparations possessing this lower melting-point can be obtained in other ways, and it is accordingly evident that gossypitrin exists in two interchangeable modifications.

Gossypitrin dissolves in alkalis with a pale yellow colouration, and gives with lead acetate a deep red precipitate. It is almost insoluble in boiling acetone, a property which readily distinguishes it from quercimeritrin, which is fairly soluble in the latter solvent.

Acetyl gossypitrin $C_{21}H_{11}O_{13}(C_2H_3O)_9$, colourless needles, melting-point 226°–228°, is almost insoluble in alcohol.

When hydrolysed with dilute sulphuric acid gossypitrin yields gossypetin and dextrose according to the equation—

$$C_{21}H_{20}O_{13}+H_2O=C_{15}H_{10}O_8+C_6H_{12}O_6$$
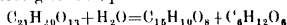
The shades given by this glucoside on mordanted wool are as follows :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Reddish-brown.	Dull yellow.	Bright orange.	Dark olive-brown.

Gossypitrin reacts, like gossypetin itself, with benzoquinone, and yields in this way a quinone to which the name *Gossypitrone* $C_{21}H_{18}O_{13}$, has been assigned. This consists of maroon-coloured needles, which possess no definite melting-point, although fusion of the product occurs about 255°–259°. By the action of warm dilute sulphurous acid solution it is reconverted into gossypitrin, and the same change appears to occur in the dyeing process, for the shades produced are identical with those yielded by this latter glucoside. It is considered probable that the sugar group of gossypitrin is attached to its tetrahydroxybenzene nucleus, though until the exact nature of this has been decided, its position is necessarily uncertain.

Isoquercitrin $C_{21}H_{20}O_{12}$, $2H_2O$, crystallises from dilute alcohol in pale yellow needles, melting at 217°–219°. It is sparingly soluble in water, and dissolves in alkaline solutions with a deep yellow tint, but its most interesting property is the fact that with aqueous lead acetate solution it gives a bright yellow precipitate entirely distinct from the deep red deposit which is produced in this manner from the isomeric quercimeritrin.

Again, though more readily susceptible to hydrolysis than the latter glucoside, it yields identical products :—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$
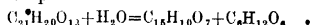
Dyeing experiments with isoquercitrin give shades entirely distinct from those given by quercimeritrin, and these, although slightly paler, resemble those yielded by quercitrin.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Brownish-yellow.	Golden-yellow.	Lemon-yellow.	Brownish-olive.

The properties of this substance indicate that its sugar group is not attached as in quercimeritrin to the phloroglucinol nucleus of quercetin. Indeed, it is probably constituted similarly to quercitrin, which, however, contains a rhamnose in the place of the glucose residue. Three formulæ are possible for isoquercitrin, which may be briefly expressed by the statement that the position of the sugar

residue in respect to the quercetin group is at one or other of the points in the following which are marked with an asterisk :—
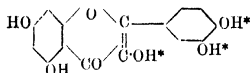
The aqueous extract of the Egyptian cotton flowers employed in this investigation gave by hydrolysis with acid 1·86 p.c of crude colouring matter, and in this approximately 10 p c. of gossypetin was present. Dyeing experiments with the flowers in the usual way gave the following shades :—

Chromium.	Aluminium.	Tin.	Iron.
Reddish-brown.	Green-yellow.	Orange-brown.	Olive-brown.

and these though duller were somewhat similar in character to those given by quercimeritrin In comparison with the shades similarly produced from other natural dyes, they most nearly resemble those of the so-called 'Patent Bark,' a preparation of quercitron bark in which quercetin and no quercitrin is present.

Among the types of cotton flowers there are (a) red, (b) pink, (c) yellow, and (d) white flowered plants In the offspring of a cross between (a) and (c) there occurs in the second and subsequent generations red and yellow plants which breed pure, whereas in the offspring of a cross between (a) and (d) all four forms occur which breed pure. As a supplementary investigation to that of the Egyptian flowers the petals derived from such pure plants occurring among the offspring of one or other of these crosses have been examined (Perkin Chem.. Soc. Trans. 1916, 109, 145) (cp. Leake, Proc. Roy. Soc. 1911, (B), 83, 147)

The types were as follows : red flowered, G. arboreum (Linn.) ; pink, G. sanguineum (Hawsk) ; yellow and white, two varieties of G. neglectum (Tod), usually now treated as one species but originally described as G. neglectum and G. rosarum. As a result it has been found that the red flowers of G. arboreum contain isoquercitrin, quercimeritrin and gossypitrin in this case being absent, whereas in the yellow flowers of G. neglectum, gossypitrin and isoquercitrin were present, and quercimeritrin appeared to be absent. On the other hand, the white flowers of G. neglectum and the pink flowers of G. sanguineum gave but traces of colouring matter too small for complete identification, though the respective products obtained resembled in their properties apigenin and quercetin. An examination of the ordinary Indian cotton flower, G. herbaceum, available only in small amount, gave the same results as the G. neglectum.

Gossypetin is also present in the flowers of the Hibiscus sabdariffa or 'red sorrel' of the West Indies, a small shrub which is widely cultivated throughout the hotter parts of India and Ceylon (Perkin, Chem. Soc. Trans 1909, 95, 1855). The stems yield the 'Rozelle hemp' of commerce, and this is obtained by retting the twigs as soon as the plant is in flower. The yellow flowers are just capable of dyeing yellow, but are not used at all in India for this purpose ; on the other hand, the red calyces are employed

for dyeing in an obscure degree in two remote parts of the country (Burkill, Agricultural Ledger, Calcutta, 1908, No. 2, 13).   A. G. P

COTTON SEED OIL is obtained on a large scale from the seeds of the several species of the cotton tree, Gossypium. In the United States, Gossypium hirsutum (Linn.), 'Upland cotton,' covered with 'linters,' is extensively cultivated, whereas the plant grown in the Sea Islands and in Egypt is G. barbadense (Linn.). The Indian variety of cotton seed is generally assumed to be G. herbaceum and G. arboreum, whilst the South American cotton plants are frequently classified as a separate species, G. acuminatum or peruvianum. Formerly the seed not required for planting was mostly wasted, as the oil contained therein could not be refined. Cotton seed oil was first expressed in this country in the year 1847. Since then the industry has assumed such enormous dimensions that the annual import of cotton seed to this country from Egypt, the East Indies, and South America amounts to more than 600,000 tons ; in addition very considerable quantities of cotton seed oil are imported from the United States, which produce almost 200,000,000 gallons of oil per annum, of which approximately 50,000,000 gallons are exported to Europe

The seed contains, on the average :—

				Per cent.
Oil	.	.	.	. 20 0
Water	.	.	.	8·5
Proteins	.	.	.	. 20·0
Carbohydrates	.	.	.	. 32·0
Crude fibre	.	.	.	. 15·0
Ash	.	.	.	. 4 5

The proportion of oil in the seed varies considerably with the origin of the seed. Thus Egyptian seed contains up to 24 p.c. of oil ; East Indian seed on the average only 18 p.c. ; American 'Uplands' and Jamaica seed 23–24 p c. ; and Brazilian and Peruvian no more than 20–21 p.c. of oil. The seeds consist on an average of 60 p c. of kernel and 40 p.c. of husk.

A distinction must be made between seed which must be decorticated before crushing, owing to the fine 'linter,' which cannot be removed readily, and seed which is crushed in the undecorticated state. Undecorticated seeds are chiefly crushed in England, France, and Germany, from Egyptian, Bombay, and also Smyrna seeds, whereas the vast majority of the American 'Upland seed' must be decorticated before being crushed. In some European establishments Bombay seed is decorticated before crushing.

The kernels ('meats') are permeated with cells containing a deep-brown colouring matter ; hence the crude cotton seed oil running from the hydraulic presses has a ruby-red to almost black colour. The depth of the colour of crude cotton oil depends, in the first instance, on the state of freshness of the seed. The American seed, which is, as a rule, crushed shortly after having been harvested, yields a crude oil of a much paler colour than that of crude oil obtained in England, France, and Germany from Egyptian seed. The palest Egyptian crude oil is obtained from fresh seed arriving in October. When the seed is stored it undergoes deterioration ('heating,' which may also occur during the voyage) ;

hence the crude oil obtained from Egyptian seed in July and August has a very dark colour.

In the American trade three grades of crude cotton seed oil are recognised, viz. 'prime,' 'choice,' and 'off' qualities. The crude oil is refined by treatment with a dilute caustic soda solution, at a temperature not exceeding 120° F., whereby the free fatty acids are neutralised; the soap so formed falls to the bottom and carries with it the brown colouring matter, so that the supernatant oil is of a bright-yellow colour. The oil is then washed free from soap, or, in the case of a technical oil, is treated with bleaching powder, to yield the bright-yellow oil of commerce. The first qualities of cotton seed oil which are not bleached with chemicals are used as edible oils, and are consumed in enormous quantities either as such, as a cooking oil, for tinning sardines, table oil, &c, or in the manufacture of lard substitutes, under such names as salad oil, sweet nut oil, butter oil. The last-named product is chiefly used in the manufactu e of margarine and compound lard

Official methods for analysing cotton seed oil, and tests for determining its behaviour when refined or bleached, have been published by the Interstate Cotton Crushers' Association, U.S.A. (Oil, Paint and Drug Rep, 1913, June 30; 1914, 33).

Cotton seed oil is, at the ordinary temperature, a pale-yellow oil of characteristic, but not unpleasant, taste. At about 12° 'stearine' deposits. This 'stearine' would interfere with the use of cotton seed oil as a table oil or salad oil; therefore the 'stearine' is removed on a large scale by cooling the oil to a low temperature, and filtering off the deposit. The filtered oil is known in commerce as 'winter oil' ('demargarinated cotton seed oil'). According to the requirements of the market, it will not 'cloud' at 40° F. or 32° F, or even at 28° F. The sp.gr. of cotton seed oil is 0·923-0·925 at 60° F The saponification value varies from 190 to 193, and its iodine value from 105 to 115.

The solid fatty acids in cotton seed oil consist chiefly of palmitic acid; small quantities of arachidic acid seem to be present, but stearic acid appears to be absent. The liquid fatty acids would seem to consist of oleic and linolic acids only.

Cotton seed oil eminently typifies a semi-drying oil. In the Livache test (see OILS AND FATS) it absorbs 5·9 p.c. of oxygen in 24 hours. By blowing air through cotton seed oil at a temperature of about 90°-100°, oxygen is absorbed, with the formation of a small amount of oxidised acids, the acetyl value of the oil rising at the same time considerably. This reaction is used on a large scale in the preparation of 'Blown Cotton Seed Oil' (see OILS AND FATS), which is used in considerable quantities as a lubricating oil in admixture with mineral oils, to produce the 'Marine Lubricating Oils' of commerce.

Cotton seed oil hardened by hydrogenation is used as a solid fat in the manufacture of margarine. A typical commercial hardened oil melts at about 38°, and has a saponification value of about 196 and iodine value of about 70.

A reliable test for the identification of cotton seed oil, and for the detection of it in other oils and fats, down to even 1 p.c. (under favour-

able circumstances), is the *Halphen* colour test, which is carried out in the following manner: 1-3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; to this is added 1-3 c.c. of carbon disulphide, holding in solution 1 p.c. of sulphur flowers. The test-tube is immersed in boiling water, or, better, in boiling brine, the carbon disulphide being allowed to evaporate off. In the course of 5-20 minutes, a deep-red colouration appears, the intensity of which stands in direct proportion to the amount of cotton seed oil in the sample. The reagent which produces the colouration appears to be an impurity in the amyl alcohol, and the test may be rendered more delicate by substituting pyridine for amyl alcohol. In this way as little as 0·25 p.c. of cotton seed oil may be detected (Gastaldi, Giorn. Farm. Chim. 1912, 61, 289). Although the test cannot be used as a quantitative one, yet it must be considered, if positive, as one of the best means of recognising the presence of cotton seed oil qualitatively. A negative Halphen test is, however, no conclusive proof of the absence of cottonseed oil in a mixture, as the colouring matter is destroyed by heating cotton seed oil to 250°, or by keeping it at 200° for some prolonged time, or by 'blowing' it. Hence 'blown cotton seed oils' do not show the Halphen colour reaction. J. L.

COTTON SEED, COLOURING MATTER OF.

Cotton seeds contain, in addition to cotton-seed oil, a phenolic substance *gossypol*, which remains dissolved in the oil when this is expressed.

By extracting the oil with caustic soda and neutralising the solution thus obtained a voluminous precipitate separates which consists of the colouring matter admixed with fatty acids, and the products of its own oxidation. For the isolation of gossypol Marchlewski (J. pr. Chem. 1899, 60, 84) employed a partially purified preparation of this character from which the main bulk of the fatty acids had been eliminated. By extraction with ether, repeated crystallisation from glacial acetic acid, and from a mixture of alcohol and 50 p.c. acetic acid, it was isolated in the form of small yellow prisms.

As the result of analyses of this substance dried *in vacuó* over sulphuric acid, Marchlewski suggested two formulæ, $C_{13}H_{14}O_4$ and $C_{32}H_{34}O_{10}$, and of these the first is considered preferable. Preparations dried at higher temperatures appeared to suffer alteration as they thus became darker, and had then a lower melting-point.

Thus the gossypol when quickly heated melted at 188°, but when previously dried at 125°-130°, at 179°-180°. It is easily soluble in the usual organic solvents, and dissolves in sulphuric acid with a cherry-red colouration, a reaction by which its presence in cotton-seed oil can be detected. In alkalis, gossypol dissolves with a yellow colouration which rapidly changes to violet, and then slowly fades. The ready susceptibility of alkaline gossypol solutions to air oxidation accounts largely for the impure nature of the crude colouring matter isolated by such reagents from the oil, and it appears that if care is taken in the process, it is possible to obtain a much cleaner material in the first instance. An alcoholic solution of gossypol gives with ferric chloride a dark-green colouration, and with the neutral and basic acetates of lead a deep-yellow precipitate. The analysis of the

lead salt corresponded to $C_{18}H_{12}O_4Pb$. According to Marchlewski, gossypol yields amorphous acetyl and benzoyl derivatives and appears to possess two hydroxyl groups. It contains no methoxy groups, and is not a glucoside. It dyes iron mordanted material a grey shade, but the product obtained by a careful oxidation of its alkaline solution possesses, it is stated, tinctorial properties of greater importance. Gossypol can be employed on cotton fabrics as a mordant for the basic colouring matters.

F. E. Carruth (Amer. Chem. J. 1918, xi. 4, 647) isolates gossypol from the decorticated cotton-seed kernels which have been crushed by rollers before they are 'cooked' in the oil mill. From these a considerable amount of oil is removed by percolation with ligroin, and the residue is then extracted with ether and the extract evaporated. The product is now treated with one-half to one-third its volume of glacial acetic acid, and on keeping for some days, or more quickly by gentle warming, crystals of *gossypol acetate* separate For purification it is dissolved in ether, glacial acetic acid is added, and the solution evaporated until crystallisation commences.

To obtain gossypol itself an ethereal solution of the acetate is treated with water, and the ether distilled off. The gossypol thus remains suspended in the water as crystalline crusts, and may be recrystallised from alcohol.

A second interesting method consists in adding aniline to an ethereal extract of cotton seed. The solution after warming on the water-bath gradually deposits on standing an orange-yellow microcrystalline precipitate, which apparently consists of an aniline salt of gossypol, $C_{30}H_{28}O_9$, $2C_6H_5NH_2$ or $2C_{30}H_{28}O_9$, $5C_6H_5NH_2$ The yield is practically quantitative, and the process may be used to estimate gossypol in extracts of cotton-seed products.

To regenerate gossypol from the aniline compound, it is dissolved in hot alcoholic potassium hydroxide, and the aniline removed by steam distillation From the alkaline liquid the gossypol is precipitated on acidification, and may be purified by conversion into the acetate according to the method given above.

Gossypol acetate, a molecular compound of gossypol and acetic acid, is evidently the substance described by Marchlewski as the 'free colouring matter. It is a comparatively stable substance, and when heated does not evolve acetic acid readily below 180°. Its formula determined by alkali titration is

$$C_{30}H_{28}O_9, C_2H_4O_2 \text{ or } C_{10}H_{30}O_9, C_2H_4O_2$$
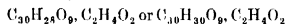
Hence gossypol itself is $C_{30}H_{28}O_9$ or $C_{10}H_{30}O_9$, and this result is in harmony with other analytical figures given in Carruth's paper.

Gossypol acetonate, $C_{30}H_{28}O_9 \cdot CH_3 \cdot CO \cdot CH_3$, is obtained as glistening crystals when gossypol is dissolved in acetone, and the solution concentrated. Like the acetate it is a stable compound, and when heated at 140°–150° it alters but little in weight.

Acetyl and benzoyl derivatives of gossypol could not be obtained in a crystalline condition, but as a result of their examination the evidence was sufficient to indicate that four or five hydroxyl groups are present in gossypol. When gossypol is heated to 186°–190° it fuses with the

evolution of vapour, and then solidifies to a black mass. On treating the residue with ether a sparingly-soluble yellow crystalline compound *B. gossypol* separates, which is much less toxic than gossypol and melts at about 246°–248°. Again, by fusion with alkali, a second new crystalline substance *C. gossypol* can be obtained, and this, which is soluble in alkalis with a blue colour is probably closely related to the purple oxidation product of gossypol referred to above.

Cotton seed meal which has been submitted to the 'cooking process' loses much of its toxic property, and contains then practically no gossypol. By extracting this product with aniline, the aniline compound of *D. gossypol* which crystallises in orange-yellow prisms can be isolated.

Alcoholic potash converts this compound into *D gossypol* itself, yellow crystals, which darken and soften at about 256°.

From the cooked meal 1·2 p c. of the aniline compound can be obtained These products have not as yet been closely examined.

A. G. P.

COUCH GRASS or Triticum, *Agropyrum B.P.*

The dried rhizome of *Agropyron repens* (Beauv). Is frequently adulterated with *Cynodon Dactylon* or dog grass A common weed in pasture and arable land Used in pharmacy. Therapeutic value obscure

COUMARANE GROUP.   Leuco-benzoyl-coumarane—

$$C_6H_5—CH \cdot OH— \text{}$$
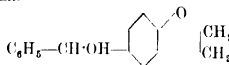
according to v Kostanecki and his co-workers is probably the mother substance of the catechin present in Gambier catechu, though the correctness of this view has not yet been fully established. *Coumarane* or *hydro-coumarone*, the inner anhydride of *o*-hydroxyphenyl ethyl alcohol -
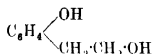
was first prepared by Alexander (Ber. 1892, 25, 2409) by reducing coumarone in alcoholic solution with sodium—
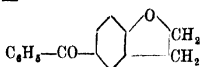

Coumarone.   Coumarane.
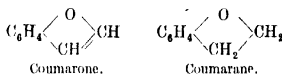
It forms a colourless oil, boiling-point 188°–189°, and gives in sulphuric acid solution by addition of ferric chloride a violet colouration. Stoermer and Göhl (Ber. 1903, 36, 2873) have obtained coumarane and its homologues by the action of sodium on *o*-bromo-phenol brom-ethyl esters according to the following equation :—
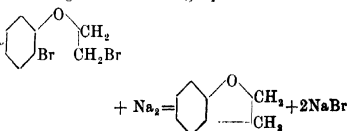
By the interaction of coumarane and benzoyl chloride in the presence of aluminium chloride

4 benzoyl-coumarane, colourless crystals, melting-point 44°—

$$C_6H_5—CO—\text{(coumarane)}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}$$

is produced (v. Kostanecki, Lampe and Marschalk, Ber. 1907, 46, 3660), and when reduced in alcoholic solution, the leuco-benzoyl-coumarane above referred to is obtained   A. G. P.

COUMARANDIONE, COUMARANONE v. KETONES.

COUMARANONE GROUP. Though colouring matters derived from coumaranone (keto-cumaran) have not as yet been isolated from natural sources, there is some probability of

Ketocumaran.   Cumaran.
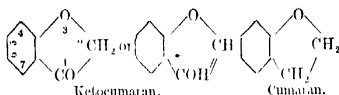
their presence in certain flowers, and they are not only historically connected with the earlier attempts to synthesise the flavones, but have in certain instances been successfully converted into flavonols.

Coumaranone (1) is obtained (Friedländer and Neudorfer, Ber. 1897, 30, 1077) by boiling acetyl o-hydroxyacetophenone bromide (2) with an aqueous suspension of chalk, or by the action of dehydrating agents on phenoxyacetic acid (3)—
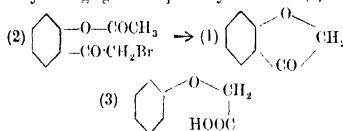
(Friedländer, Ber. 1899, 32, 1867), and consists of colourless needles, melting-point 97°. It condenses with benzaldehyde in the presence of hydrochloric acid with formation of benzylidene-coumaranone—
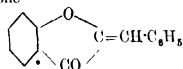
which was at first considered by Friedländer and Neudörfer (Ber. 1897, 30, 1077) to consist of flavone. On substituting protocatechuic aldehyde for benzaldehyde these authors obtained the dihydroxy compound—
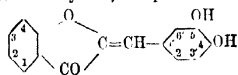
and this is a strong dyestuff which gives on aluminium mordanted fabrics an orange, and with iron and chromium mordants brown-coloured shades.

The first colouring matter of this group was, however, prepared in 1896 by Friedländer and Rüdt (Ber. 29, 878) from chlorogallacetophenone and benzaldehyde—
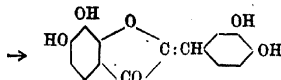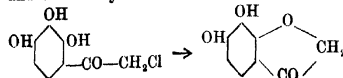
and from the analogous resacetophenone derivative other hydroxy compounds of this group were obtained later. These are of an orange or orange-red colour, as a rule form oxonium salts, and those possessing tinctorial property dye alum mordant a much more orange shade than the flavone colouring matters. There is indeed a close resemblance in this latter respect between these compounds and the colouring matters derived from chalkone—
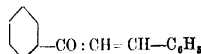
(Perkin, Chem. Soc. Trans. 1904, 85, 1465), for butein (a tetrahydroxy chalkone obtained from the *Butea frondosa*) and the 3 : 4 : 3′ : 4′ tetra-hydroxybenzylidene coumaranone of Friedländer and Rudt give almost identical shades. The benzylidene coumaranones dissolve in sulphuric acid with the production of a red or red-violet colouration, and can thus again be distinguished from flavones which in this manner give either colourless or pale yellow solutions.

In 1896 Kesselkaul and v. Kostanecki (Ber. 29, 1886) suggested that judging by its colour reactions the colouring matters of Friedländer and Rudt were not, as these authors suggested, flavone but rather coumaranone derivatives, and the true constitution of these substances became evident on the synthesis of flavone itself by Feuerstein and v. Kostanecki (*l.c.*). That benzylidenecoumaranones can be converted into flavanol derivatives has been shown by Auwers and Müller (Ber. 1908, 41, 4203), and this transformation is discussed under FLAVONOL.

Coumaranone is also interesting as the source of ox-indigo—
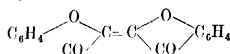
the oxygen analogue of indigotin. This crystallises in yellow prisms, but does not possess any tinctorial value.

Analogous colouring matters can be obtained from diketohydrindene (indandione), this also possessing the reactive methylene group, with aldehydes. Thus by heating this compound with protocatechuic aldehyde at 110°–120° v. Kostanecki prepared the dihydroxybenzylidene derivative—
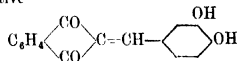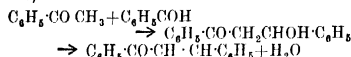

which consists of brownish-yellow needles, melting-point 257°, soluble in alkaline solutions with a red-violet colour and gives yellow shades on aluminium mordanted fabrics.

From indoxyl also in a similar way Perkin and Thomas (Chem. Soc. Trans. 1909, 95, 798) prepared dihydroxybenzaldehydeindogenide—
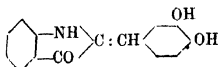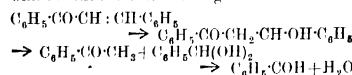
crystallising in orange-red needles, and producing with aluminium mordanted fabrics dull scarlet shades.

Chalkone or benzylideneacetophenone is readily prepared by the interaction of acetophenone and benzaldehyde (Claisen, Ber. 20, 257)—

$$C_6H_5 \cdot CO \cdot CH_3 + C_6H_5COH$$
$$\rightarrow C_6H_5 \cdot CO \cdot CH_2CHOH \cdot C_6H_5$$
$$\rightarrow C_6H_5 \cdot CO \cdot CH \cdot CH \cdot C_6H_5 + H_2O$$

It consists of yellow rhombic prisms, melting-point 57°–58°.

When submitted to hydrolysis it is reconverted into the aldehyde and ketone, a reaction which is the reversal of that given above—

$$C_6H_5 \cdot CO \cdot CH : CH \cdot C_6H_5$$
$$\rightarrow C_6H_5 \cdot CO \cdot CH_2 \cdot CH \cdot OH \cdot C_6H_5$$
$$\rightarrow C_6H_5 \cdot CO \cdot CH_3 + C_6H_5CH(OH)_2$$
$$\rightarrow C_6H_5 \cdot COH + H_2O$$

By the employment of hydroxyacetophenones and hydroxybenzaldehydes, in general previously methylated, numerous chalkone derivatives have been obtained by v. Kostanecki and his co-workers. Only one natural colouring matter of this group, known as *butein*, has at present been isolated, and the synthetically prepared compounds have been more specially interesting owing to their employment for the synthesis of the flavonol group of colouring matters.

Ryan and O'Neill by the aid of diacetoresorcinol have obtained dichalkone compounds. Thus diacetoresorcinol dimethyl ether and benzaldehyde form dibenzylidenediacetoresorcinol dimethyl ether, and this by the action of aluminium chloride is demethylated with production of the free hydroxy compound—

$$C_6H_5 \cdot CH : CH - CO - \underset{OH}{\overset{OH}{\bigcirc}} - CO - CH \cdot CH \cdot C_6H_5$$
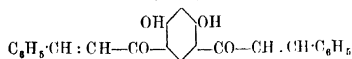
It was obtained as yellow crystals melting at 196°–198°.

Interesting is the fact shown by these authors that by a variation in its method of preparation four distinct varieties of this dichalkone can be produced. Whereas three of these designated as α, β and δ are stereo-isomers, the fourth or γ variety is structurally related to the other three.

When 2-hydroxychalkone is digested at the boiling temperature with alcoholic sulphuric acid, *flavanone* (dihydroflavone) is produced according to the following scheme :—
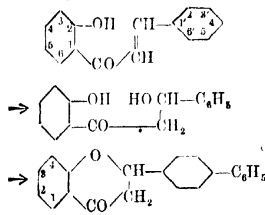
and this is the method generally adopted for the synthesis of flavanone derivatives. On the other hand, though as a rule a chalkone only is produced by the interaction of aldehyde and
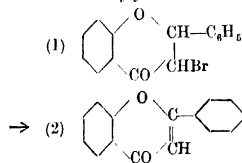
hydroxyketone, when gallacetophenone dimethyl ether (Woker, v. Kostanecki, and Tambor, Ber. 1903, 36, 4235) or quinacetophenone monomethyl ether (v. Kostanecki and Lampe, *ibid.* 1904, 37, 773) are condensed with benzaldehyde in the presence of sodium hydroxide the respective flavanones (1 and 2) are thus directly obtained—
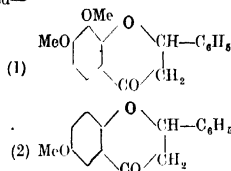
On hydrolysis the flavanones yield chalkones, a reversal of the equation given above. The reaction in these cases is not unidirectional, and the conversion of flavanone into chalkone, or chalkone into flavanone, is never complete.

Chalkones which contain hydroxyls in the ortho position to one another, in the position 3′·4′ are powerful colouring matters, whereas flavanones possessing similar hydroxyls are not dyestuffs, as indeed their constitution indicates. During the dyeing operation, employing mordanted woollen material hydrolysis occurs, with subsequent chalkone production, and the shades produced by them are in reality those derived from the latter. Flavanone crystallises in small colourless needles, melting at 75°–76°.

Bromflavanone (1) by elimination of hydrobromic acid readily yields flavone (2)—
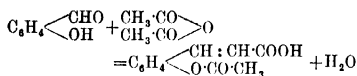

and, again, flavanones may be converted into flavonols.   · A. G. P.

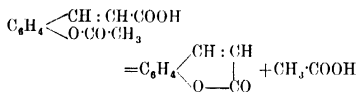**COUMARIN** $C_9H_6O_2 = C_6H_4 \Big\langle \begin{smallmatrix} CH : CH \\ | \\ O - CO \end{smallmatrix}$ (1, 2)
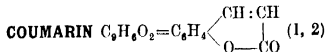
was obtained by Vogel (Gilb. Ann. 64, 161), in 1820, from the tonka bean (the seed of *Dipteryx (Coumarouna) odorata*, Willd.), or from the melilot (*Melilotus officinalis*, Lam.), and from the woodruff (*Asperula odorata*, Linn.), but was mistaken by him for benzoic acid. Guibort, however, showed that the crystalline odoriferous principle of the tonka bean was distinct from benzoic acid, and named it *coumarin*. It occurs in *Peristrophe angustifolia* (Nees), *Achylis triphylla* (DC.), and in many other plants, and is a normal constituent of lavender oil. It is present in plants as a glucoside, which is decomposed by a ferment present in the plant. This ferment is destroyed by alcohol or boiling water (Molish, J. Pharm. Chim. 1902, 279).

It was first obtained synthetically by Perkin by heating the sodium compound of salicylaldehyde with acetic anhydride (Chem. Soc. Trans.

1863, 53); or more simply by boiling together salicylaldehyde, acetic anhydride, and dry sodium acetate (*ibid.* 1887, 388; see also Tiemann and Herzfeld, Ber. 1877, 284). Acetyl coumaric acid is first formed:

$$C_6H_4{<}{}^{CHO}_{OH} + {}^{CH_3 \cdot CO}_{CH_3 \cdot CO}{>}O$$

$$= C_6H_4{<}^{CH : CH \cdot COOH}_{O \cdot CO \cdot CH_3} + H_2O$$

which then parts with acetic acid, yielding coumarin:

$$C_6H_4{<}^{CH : CH \cdot COOH}_{O \cdot CO \cdot CH_3}$$

$$= C_6H_4{<}^{CH : CH}_{O \longrightarrow CO}{\Big|} + CH_3 \cdot COOH$$

By treating salicylaldehyde (1 molecule) with excess of acetic anhydride (4 molecules) for 6 hours at 180°, coumarin is formed (Reychler, Bull. Soc. chim. 1897, 17, 517)

Coumarin is also formed in small quantity by heating a mixture of phenol and malic acid with sulphuric acid

$$C_6H_5 \cdot OH + {}^{CH_2COOH}_{CH(OH) \cdot COOH}{\Big|}$$

$$= C_6H_4{<}^{CH : CH}_{O \longrightarrow CO}{\Big|} + CO + 3H_2O$$
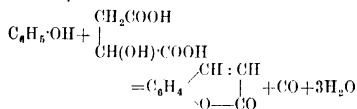
(Von Pechmann, Ber 1883, 2119; 1884, 929, 1649)

It has also been obtained from *o*-chlorocinnamic acid which is reduced electrolytically to *o*-chloro-hydrocinnamic acid and then heated with aqueous sodium hydroxide to 250°, when melilotic acid is produced. Thionylchloride converts melilotic acid into melilotic anhydride, from which coumarin results by oxidation with bromine vapour at 270°–280° (Meyer, Beer and Lasch, Monatsh. 1913, 34, 1665).

Substituted coumarins may be obtained by condensing phenols with acetoacetic ester or with malic acid in the presence of concentrated sulphuric acid.

The condensation of acetoacetic ester or malic acid with substituted phenols (containing alkyl, hydroxyl or dialkyl-amino groups) gives good yields if the groups are present in the positions as shown—

The condensation is, however, prevented by the presence of nitro, carboxyl or carbethoxy groups (Clayton, Chem. Soc Trans., 1908, 2018). It is also very considerably affected by the concentration of the sulphuric acid used.

Coumarin forms rhombic crystals melting at 70°; boils at 290°–290·5°; has a pleasant, aromatic odour; is scarcely soluble in cold water, readily soluble in boiling water, very soluble in alcohol and ether. Crude coumarin may be purified by repeated boiling with light petroleum (Claassen, Pharm. J. 1897, 161).

It dissolves in caustic alkalis, and is reprecipitated on addition of acids. If, however, it is heated for some time with concentrated

caustic alkali, or better, with sodium ethoxide, a solution is formed from which acids precipitate

$$coumaric\ acid\quad C_6H_4{<}^{CH : CH \cdot COOH}_{OH}\quad (1, 2).$$
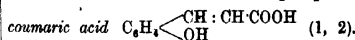
This compound can be reconverted into coumarin by heating it with acetic anhydride; but when heated alone it is decomposed, yielding phenol and other substances. Reduction of coumarin with zinc in alkaline solution or sodium amalgam in aqueous solution yields melilotic acid as the chief product; with sodium amalgam and alcohol hydrocoumaric acid is formed (Williamson, J. 1876, 587).

On account of the differences shown between coumarin and thiocoumarin, it has been suggested that the two compounds should be represented by the annexed formulæ:


(Clayton, Chem. Soc. Trans. 1908, 524).

The *thiocoumarin* is produced by heating coumarin with phosphorus pentasulphide, and in contradistinction to coumarin is coloured. It also reacts with phenylhydrazine, yielding coumarin phenylhydrazone (with elimination of hydrogen sulphide), which cannot be obtained directly from coumarin itself. For an account of the synthetic benzotetronic acids (hydroxy-coumarin carboxylic acids), *see* Anschütz, Annalen, 367, 174.

In Germany, woodruff (Ger. *Waldmeister*) is steeped in white wine, to which it imparts the pleasant aroma of coumarin (*Maiwein, Maitrank*). Instead of woodruff, an alcoholic solution of coumarin is employed for the same purpose under the name of *Maiweinessenz*. In larger doses coumarin is stated to have a narcotic action.

Coumarin has the agreeable odour of asperula, and is used in perfumery for the preparation of asperula essence. It is also frequently used to adulterate extract of vanilla (*q.v.*) (*v.* LACTONES).
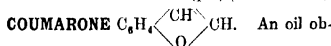
COUMARONE $C_6H_4{<}^{CH}_{O}{>}CH$. An oil obtained from the coal-tar fraction boiling between 165° and 175°. After the pyridine bases and phenols have been removed by acid and alkali, it is obtained as the dibromide on addition of bromine. The dibromide is reduced to coumarone by alcoholic potash and sodium amalgam (Kraemer and Spilker, Ber. 1890, 78). It can also be obtained from this source by adding picric acid to the mixture of oils, whereby the picrate of coumarone crystallises out. This is separated, decomposed by hot water or dilute alkali, and the coumarone obtained by steam distillation. The picric acid is recovered and used for another operation (Ch. Fab. Act. ges. Hamburg, Eng. Pat. 1422; D. R. P. 53793; Ber. 1891, Ref. 233). Coumarone has been synthesised by heating *o*-hydroxy-ω-chlorcinnamene OH·C$_6$H$_4$·CH : CHCl with potash, hydrogen chloride being eliminated (Komppa, Ber. 1893, 2968). It has also been prepared by heating phenoxyacetaldehyde with zinc chloride in glacial acetic acid (Stoermer, *ibid.* 1897, 1700).

Coumarone boils at 174·0° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1249). It is unacted

upon by potash or by hydrochloric acid. Sulphuric acid reacts with coumarone in benzene solution, producing a soluble resinous material *paracoumarone* $(C_9H_6O)_4$, which is used to preserve wood and paper. Other polymerides are known. Coumarone is of interest as, when passed through a red-hot tube with benzene, phenanthrene is produced, and with naphthalene, chrysene is produced (Kraemer and Spilker, Ber. 1890, 84). The methyl coumarones are present in the coal-tar fraction of b p. 185°–195° (Stoermer and Boes, *ibid.* 1900, 3013).

COUMARONE RESINS. Technical Coumarone resins are prepared by treating solvent naphtha with sulphuric acid. They differ from the pitches by their ready solubility in acetone, and from the condensation products of phenols with formaldehyde by their solubility in petroleum spirit and by not yielding phenol when heated with soda-lime at 260°. They differ from the natural resins in being optically inactive, in having a lower melting-point, saponification value and iodine value. They are classified for commercial purposes according to their colour and hardness; those softening above 50° are termed 'very hard,' between 40° and 50° 'hard,' and between 30° and 40° 'medium hard' For methods of their examination, *see* Marcusson, Chem Zeit 1919, 43, 109–122; Analyst, 1919, 44, 203.

If coumarone resins are distilled under ordinary or under reduced pressure they yield yellow oils between 150° and 240°, consisting mainly of coumarone, or partially depolymerised paracoumarone, together with indene hydrindene and small quantities of phenol By treatment with condensing agents and catalysts these oils again yield resins varying in character with the nature of the catalyst. Coumarone oils are not autoxidisable like drying oils, but when mixed with 4–6 p.c. of driers, such as the resinates of lead or manganese, they yield dry films. The distinctive oxidation process of coumarone oils is to be attributed to indene (E Stern, Zeitsch. angew. Chem. 1919, 32, 246)

COUPIER'S BLUE *v.* INDULINES.

COVELLITE. Native cupric sulphide, CuS, crystallising in the hexagonal system. Crystals are rare and have the form of thin six-sided plates. Fine large crystals have been found at Butte in Montana. The mineral has a characteristic indigo-blue colour, hence the name *indigo-copper* (German, *Kupferindig*). It occurs in most copper-mines as a blue, earthy coating on other sulphide ores of copper, and is sometimes found in sufficient quantities to be of importance as an ore, *e.g.* at Butte in Montana, and Copiapo in Chile. Covellite containing platinum (as the mineral sperrylite, PtAs₂) is mined in the Medicine Bow Mountains in Wyoming.

L. J. S.

COW TREE WAX *v.* WAXES.

COXPYRIN. Syn. for acetyl salicylic acid.

CRANBERRY, the fruit of *Vaccinium Oxycoccos* (Linn.).

American analyses give as the average composition of the berries :

Water	Protein	Fat	Carbohydrates	Ash
88·5	0·5	0·7	10·1	0·2

König gives :

Water	Protein	Free acid	Sugar	Other carbohydrates	Ash
89·6	0·12	2·3	1·5	6·3	0·15

The juice of cranberries was examined by Mach and Portele in 1888 (Landw. Versuchs. Stat. 1889, 38, 69), who found a litre of the fresh juice to contain (in grammes)

Invert sugar	Acidity (as malic acid)	Benzoic acid	Tannic acid	Ash	Nitrogen
87·1	19·0	0·75	2·2	3·0	0·11

The sp.gr. of the juice averaged 1·0591.

The juice will not ferment with yeast, owing, it is said, to the presence of benzoic acid, but this may be due to the poverty of the juice in nitrogenous matter, for Otto (Bied. Zentr. 1899, 28, 284) found that bilberry juice would only ferment vigorously with yeast after the addition of asparagine (about 0·6 gram per litre) or of ammonium chloride (about 0·3 gram per litre).

Rising (Bied. Zentr. 1915, 44, 163) found in cranberries, benzoic, isovaleric, malic and citric acids, fermentable sugars and a glucoside— *vaccinin* $C_6H_{11}O_5·Bz$. The amount of sugar varied from 5·7 to 10·4 p.c., and that of benzoic acid from 0 108 to 0·455 p c. The keeping qualities of the fruit are dependent upon the amount of benzoic acid present

The pigment of the cranberry consists of an anthocyanin—a compound of galactose with a cyanidin, the chloride of which has the composition $C_{15}H_{11}O_6Cl$ (Willstatter, Sitzungber. K Acad. Wiss Berlin, 1914, 12, 402).

Claassen (*ibid.* 16, 70) isolated a bitter substance from cranberries, to which he gave the name *oxycocin*, and which he found to give reactions similar to those of arbutin $C_{12}H_{16}O_7$, occurring in the leaves of the red bearberry, *Arctostaphylos Uva-ursi* (Spreng.).

The ash of cranberry juice contains about 3 p.c. of phosphorus pentoxide and 47 p.c. of potash.

H. I.

CREAM OF TARTAR *v.* TARTARIC ACID.

CREATINE, *Methylglycocyamine, Methylguanidoacetic acid* $H_2N·C(NH)NMe·CH_2·CO_2H, H_2O$ discovered by Chevreul (Annalen, 1835, 4, 293) in muscular flesh ($\chi\rho\epsilon as$=flesh), occurs in human flesh, in the flesh and blood of many warm and cold blooded animals and in urine (Liebig, Annalen, 1847, 62, 257 ; Gregory, *ibid.* 1848, 64, 105 ; Schlossberger, *ibid.* 1848, 66, 80 ; Voit, Z. Biol. 1868, 4, 77 ; Price, Chem. Soc. Trans. 1851, 3 ; Marcet, *ibid.* 1864, 2, 406 ; Folin and Denis, J. Biol. Chem. 1914, 17, 488 ; Rose, *ibid.* 1911, 10, 265) ; the amount varies with the species and the organ ; the flesh of fowl yields 3·21 p c. ; of pigeon, 0·825 p.c. ; of ox, 0·697 p.c. ; of ox heart, 1·375 p.c. ; of herring, 1·324 p.c. ; and of brill, 0·614 p.c. (Gregory, *l.c.* ; Beker, Zeitsch. physiol. Chem. 1913, 87, 28 ; according to Myers and Fine (J. Biol. Chem. 1913, 14, 9–12) it is constant for a given animal Okuda, 8th Int. Cong. App. Chem. 1912, 18, 275.

According to Folin (Amer. J. Physiol. 1905, 13, 45, 66, 117), van Hoogenhuyze and Verploegl (Zeitsch. physiol. Chem. 1908, 57, 161), Mellanby (J. Physiol. 1908, 36, 447), muscular creatine has its origin in the liver. This organ is continuously forming creatinine from substances carried to it by the blood from other organs, and in the developing muscle. This is changed to creatine, until the muscle is saturated with creatine, when the excess of creatinine is excreted by the kidneys. *Cf.*, however, Folin

and Denis (*ibid.* 493-496 and 500-501) who suggest that creatine is part of living vertebrate protoplasm and the creatine of muscles a post-mortem product, and that creatinine elimination is a measure of the total normal tissue metabolism and independent of any special function of the liver; *see also* Myers and Fine (*ibid.* 1913, 15, 283-285 and 301-304); Inooye (Zeitsch. physiol. Chem. 1912, 81, 71-79); Rieser (*ibid.* 1913, 86, 415-453, and 1914, 90, 221-235); Myers and Fine (*ibid.* 1913-14, 16, 169, and *ibid.* 1915, 21, 377); Rose and Dimmitt (J. Biol. Chem. 1916, 26, 345); Baumann and Hines (J. Biol. Chem. 1917, 31, 549) The creatine is presumably combined with the muscular protoplasm, for though a readily dialysable substance, it does not pass into the surrounding lymph or blood *in vitro*, nor is it readily obtainable by diffusion from muscular flesh (Urano, Beitr. Chem. physiol. Path. 1907, 9, 104). *Cf.*, however, Folin and Denis (J. Biol. Chem. 1914, 17, 499); Leo and Howe (Pro Amer. Soc. Biol. Chem. 1912-13, xliii. For the origin of urinary creatine, *see* Benedict and Osterberg (J. Biol. Chem. 1914, 18, 195), Myers and Fine (*ibid.* 1913, 15, 301)

In order to extract creatine, the flesh is heated with its own weight of water at 60°, and the juice expressed The flesh extract is then heated to coagulate the protein, and filtered; the filtrate is treated with basic lead acetate until no further precipitation occurs, and again filtered after removing the excess of lead from the filtrate by sulphuretted hydrogen, when it is evaporated until creatine separates on cooling; this is washed with alcohol and recrystallised from water (Neubauer, Zeitsch anal Chem. 1863, 2, 26; 1867, 6, 33). Creatine may be prepared by the decomposition of creatinine zinc chloride by means of calcium hydroxide (Benedict, J. Biol. Chem. 1914, 18, 186).

Creatine is prepared synthetically by heating sarcosine with cyanamide at 100°.

$$CN \cdot NH_2 + NHMe \cdot CH_2 \cdot CO_2H$$
$$= NH : C(NH_2) \cdot NMe \cdot CH_2 \cdot CO_2H$$
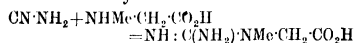
(Volhard, Z. Chem. N F. 1869, 5, 318; Strecker, J. 1868, 686); or, together with creatinine, by fusing sarcosine with guanidine carbonate (Paulmann, Beilstein Suppl. 1. 657).

Creatine forms colourless transparent monoclinic prisms, containing $1H_2O$, which it loses at 100°; it dissolves in 74·4 parts of water at 18°; or in 9810 parts of cold absolute alcohol, and is insoluble in ether (Liebig, Annalen, 1847, 62, 257). Heat of combustion at constant pressure is 4240 calories (Emery, Benedict, Amer J. Physiol. 1911, 28-307). The presence of urea, creatinine, or certain salts, raises the solubility of creatine in water and alcohol (Neubauer, *l.c.*). The aqueous solution is neutral, and has a bitter, harsh taste.

Creatine is decomposed by boiling baryta water into sarcosine, urea, and methylhydantoïn

$$NH:C(NH_2) \cdot NMe \cdot CH_2 \cdot CO_2H + H_2O$$
$$= CO(NH_2)_2 + NHMe \cdot CH_2 \cdot CO_2H$$

$$CO(NH_2)_2 + NHMe \cdot CH_2 \cdot CO_2H \rightarrow CO \begin{array}{c} NMe \cdot CH_2 \\ | \\ NH \cdot CO \end{array}$$
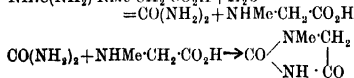
(Neubauer, Annalen, 1866, 137, 294); or by mercuric oxide and water into oxalic acid and methylguanidine; or by heating with soda-lime into ammonia and methylamine. Treated with mercuric acetate in presence of sodium carbonate it yields *α-methylguanidinoglyoxylic acid* $NH_2 \cdot C(NH) \cdot NMe \cdot CO \cdot CO_2H, 2H_2O$; glistening flakes, m.p. 203°-204° (Baumann and Ingvaldsen, J. Biol. Chem. 1918, 35, 277). When potassium hydroxide is added to an aqueous solution of creatine and silver nitrate until the white precipitate first formed just redissolves, the liquid solidifies to a transparent gelatinous mass immediately reduced on heating, or in the course of a few hours at the ordinary temperature. The addition of potassium hydroxide to a solution of creatine and mercuric chloride precipitates a white crystalline compound ($C_4H_8O_2N_3)_2Hg,HgO$ (Engel, Compt. rend 1874, 78, 1707; 1875, 80, 885) Creatine is converted into creatinine by heating with dilute mineral acids for some hours (Dessaignes, J. 1857, 544), or at 117° for 15 minutes (Benedict and Myers, Amer. J. Physiol. 1907, 18, 362); or by boiling down to dryness the solution of creatine to which has been added an equal volume of hydrochloric acid (Benedict, J. Biol. Chem. 1914, 18, 192); or by heating with water only in sealed tubes at 100° for 2-3 days (Neubauer, Zeitsch anal Chem. 1863, 2, 33). Smorodincev (J. Russ Phys Chem. Ges. 1915, 47, 1275-9) obtained a double salt of silver nitrate and creatinine, $C_4H_7ON_3 \cdot AgNO_3$ (decomposes 188°-191°) on treating pure creatine with silver nitrate in a slightly acid solution.

Creatine forms soluble normal salts with the mineral acids (Dessaignes, Annalen, 92, 409), and readily soluble compounds with zinc chloride $C_4H_9O_2N_3, ZnCl_2$; and cadmium chloride $C_4H_9O_2N_3, CdCl_2, 2H_2O$ (Neubauer, *ibid.* 137, 300).

Creatine is not usually estimated directly; it is converted into creatinine (*q.v.*), and estimated as such; for the estimation of creatine in urine, *v.* Benedict (J. Biol. Chem. 1914, 18, 192) and Walpole (J. Physiol. 1911, 42, 301), who makes use of the fact that a pale red colour is given by alkaline solutions of creatine and not by creatinine when a trace of diacetyl is added. For its estimation in blood *v.* Greenwald (Proc. Soc exp. Biol. Med. 1917, 14, 115).

α-Guaninopropionic acid, alacreatine

$$NH_2 \cdot C(NH)NH \cdot CHMe \cdot CO_2H$$

from alanine and cyanamide (Baumann, Annalen. 1873, 167, 83), an isomeride of creatine forms, sparingly soluble prisms.

The homologues of creatine are prepared by the action of cyanamide on the corresponding amino-acid in the presence of ammonia, *e.g.* *α-aminocaproycyamine*

$$NH_2 \cdot C(NH)NH \cdot CH(CO_2H)CH_2 \cdot CHMe_2$$

from leucine and cyanamide (Duvillier, Compt. rend. 1886, 103, 211; 1887, 104, 1290). According to Duvillier (*l.c.*) methyl- or ethylamino-acids yield with cyanamide the corresponding *creatinine*. The *creatine* is formed only in the case of methylglycocine and β-methyl-aminopropionic acid, the latter yielding *methyl-alacreatine* $NH_2 \cdot C(NH) \cdot NMe \cdot CHMe \cdot CO_2H$ (Lindenberg, J. pr. Chem. 1875, [2] 12, 253). This generalisation is not confirmed by Gansser (Zeitsch. physiol. Chem. 1909, 61, 16), who obtained the creatinine and not the creatine
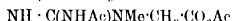
from α-methylaminopropionic acid and cyanamide, but prepared β-*methylguaninopropionic acid* $NH_2 \cdot C(NH)NMe \cdot [CH_2]_2CO_2H, H_2O$, m.p. 201°–202°, from cyanamide and β-methylaminopropionic acid, and γ-*methylguaninobutyric acid* $NH_2 \cdot C(NH)NMe \cdot [CH_2]_3CO_2H$, m.p. 307°, from cyanamide and γ-methylaminobutyric acid.

Formaldehyde and creatine yield the *compound* $C_6H_{11}O_3N_3, 2H_2O$, decomposing at 250°, and forming a *dibenzoyl derivative* $C_6H_9O_3N_3Bz_2$, m.p. 265°–266° (Jaffé, Ber. 1902, 35, 2896).

Phthalyldicreatine

$$C_6H_4[CO \cdot NH \cdot C(NH) \cdot NMe \cdot CH_2 \cdot CO_2H]_2$$
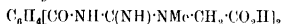
has m.p. 212° (Urano, Beit. Chem. Physiol. Path 1907, 9, 183). *Diacetylcreatine*

$$NH \cdot C(NHAc)NMe \cdot CH_2 \cdot CO_2Ac$$

has m.p. 165° (Erlenmeyer, Annalen, 1895, 284, 50). M. A. W.

CREATININE, *Methylglycocyamidine*
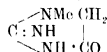
discovered by Liebig in human urine (Annalen, 1847, 62, 268), the amount excreted being 26–30 mg. per kilo weight of body per diem (Koch, Amer. J. Physiol 1905, 15, 1), is also a constant constituent of the urine of horses, cows, dogs, pigs, and rabbits ; it is found in muscle (Shaffer and Reinoso, Proc Soc Biol. Chem. 1910, 7, xxx. ; Meyers and Fine, J Biol Chem. 1915, 21, 383) and occurs in small quantities in the flesh of fish, about 0 2 p c in the case of cod (Poulsson, Chem Zentr 1904, ii 30) ; for other estimations, *see* Okuda (8th Int. Cong. App. Chem, 1912, 18, 275) ; and traces (0·000098 p c , Cooper Colls, J. Physiol 1896, 20, 107) are found in the blood. According to Folin and Denis (J Biol Chem. 1914, 17, 487) normal human blood contains 1 mg creatinine and 6–8 mg. of creatinine and creatine per 100 grs. blood. In domestic animals it is about the same ; in birds 0 1 mg creatinine but 11 mg creatinine and creatine. It is probably a normal constituent of all soils (Shorey, J Amer Chem. Soc. 1912, 34, 99–107 ; Sullivan, J. Amer. Chem. Soc. 1911, 33, 2035–42) and vegetable matter (Oshima and Ariizumi, J Coll. Agric. Tohoku Imp. Univ. 1914, 6, 17–25).

Under normal conditions, the excretion of creatinine is constant from day to day and hour to hour (Shaffer, Amer. J. Physiol. 1908, 23, 1) ; it is not affected by diet or exercise (Folin, *ibid.* 1905, 13, 45, 66, 117 ; Pekelharing, van Hoogenhuyze Verploegh. Proc. k. Akad. Wetensch, Amsterdam, 1905, 8, 363 ; Klercker, Beit. Chem. Physiol. Path. 1906, 8, 59). It is now generally regarded as one of the end products of endogenous nitrogenous katabolism, the liver continuously forming creatinine from substances carried to it by the blood ; *cf.*, however, Folin and Denis (J. Biol. Chem. 1914, 17, 500–501) ; part of this creatinine furnishes the muscular creatine by the change it undergoes in the developing muscle, *v.* CREATINE ; the rest is excreted by the kidneys (Folin, *l.c.* ; Mellanby, J. Physiol. 1908, 36, 447 ; Lefmann, Zeitsch. physiol. Chem. 1908, 57, 476). In cases of fever or starvation, the amount of urinary creatinine is increased, the material wanted for contraction

being drawn from the muscular proteids (Pekelharing, van Hoogenhuyze Verploegh, *l.c.* ; Leathes, J. Physiol. 1907, 35, 205). In cancer of the liver, the urinary creatinine is diminished and the creatine is increased (Mellanby, *loc. cit.*).

Creatinine is extracted from urine by evaporating to one-third the original volume, decanting from the salts that crystallise out, precipitating with lead acetate and filtering, removing the lead from the filtrate and precipitating the creatinine as the sparingly soluble double salt with mercuric chloride. This is separated, decomposed by sulphuretted hydrogen, and the creatinine crystallised from the filtrate as the hydrochloride (Maly, Annalen, 1871, 159, 279) , or by precipitating it as creatinine potassium picrate with subsequent decomposition of the double salt (Folin, J. Biol. Chem. 1914, 17, 463–467 ; Benedict, *ibid.* 1914, 18, 184–190).

For extraction from the body tissues and fluids, *see* Costantino (Chem Zentr. 1915, 11, 287, from Arch farm. sper 1915, 19, 254–258.)

Creatinine bears the same relation to creatine as hydantoïn to hydantoïc acid
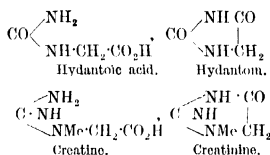
and is prepared by boiling creatine with dilute mineral acids for some hours (Liebig, Annalen, 1847, 62, 628) or by heating at 117° for 15 minutes under pressure (Benedict and Myers, Amer. J. Physiol. 1907, 18, 362), or by boiling down to dryness with an equal volume of hydrochloric acid (Benedict, J. Biol. Chem. 1914, 18, 192).

Creatinine can be prepared synthetically by heating guanidine carbonate with sarcosine at 140°–160° (Horbaczewski, J. Pharm. Chim. 1885, 86). A quantitative yield is obtained by heating N-methylglycocyamine with an organic acid (D. R. P. 281051, from J. Soc. Chem. Ind. 1915, 34, 637).

By heating creatinine with silver nitrate and baryta in excess on the water-bath for about an hour a nearly quantitative yield of methyl guanidine can be obtained (Ewins, Bio-Chem. J. 1916, 10, 104). By oxidation with mercuric acetate it yields α-methyl guanidinoglyoxylic acid (Baumann and Ingvaldsen, J. Biol. Chem. 1918, 35, 277).

Creatinine forms anhydrous monoclinic prisms soluble in 11·5 parts of water or 100 parts of absolute alcohol at 16° (Liebig, *l.c.*), and separates on slow evaporation of dilute solutions in square plates containing $2H_4O$ (Salkowski, Zeitsch. physikal. Chem. 1880, 4, 133). It is a weak base, displacing ammonia from its salts, and forming soluble salts with the mineral acids (Liebig, *l.c.*), the *picrate* $C_4H_7ON_3 \cdot C_6H_3O_7N_3$, m.p. 212°–213°, crystallises in sparingly soluble yellow needles ; the *acid picrate*

$$C_4H_7ON_3 \cdot 2C_6H_3O_7N_3$$
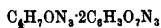
has m.p. 161°-166° (Mayerhoffer, Wien. Klin. Woch. 1909, 22, [3]); the *tartrate*

$$(C_4H_7ON_3)_2 \cdot C_4H_6O_6$$
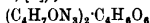
decomposes at 207°-209°; the *oxalate*

$$(C_4H_7ON_3)_2 \cdot C_2H_2O_4$$
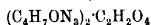
is sparingly soluble in alcohol (Poulsson, Chem. Zentr. 1904, ii. 30). Creatinine forms characteristic double salts with platinic chloride $(C_4H_7ON_3,HCl)_2 \cdot PtCl_4$, orange-red plates, m.p. 220°-225°; with auric chloride

$$C_4H_7ON_3 \cdot HCl \cdot AuCl_3$$
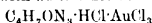
yellow crystals, m.p. 170°-174°; with potassium picrate $C_4H_7ON_3 \cdot C_6H_3O_7N_3 \cdot KC_6H_2O_7N_3$, lemon-yellow prisms, 100 parts of water dissolve 0 1806 part of the salt at 19°-20°; with zinc chloride $(C_4H_7ON_3)_2 \cdot ZnCl_2$, almost insoluble in alcohol (Heintz, J. 1847, 48, 883); with mercuric chloride $4(C_4H_5HgON_3 \cdot HCl) \cdot 3HgCl_2, 2H_2O$ (Johnson, Proc. Roy. Soc 1886, 43, 493).

Creatinine is converted into creatine by the action of cold dilute ammonia or calcium hydroxide solutions; or on treatment with iodine (Reichardt, Pharm. Zeit. 1911, 56, 922); boiling baryta solution converts it into ammonia and methyl hydantoïn; with alkaline oxidising agents it yields methylguanidine and oxalic acid, but is comparatively stable towards acid permanganate solutions (Jolles, Ber. 1902, 35, 160).

The presence of creatinine in dilute solution or in urine can be detected by (1) Maschke's test (Zeitsch. anal. Chem. 1878, 134), which consists in the formation of a sparingly soluble double compound of creatinine and cuprous oxide, when the suspected solution is heated at 50°-60° with Fehling's solution; as the cuprous oxide is formed by the oxidation of part of the creatinine, it is advisable to add a little glucose to the mixture; the test is sufficiently delicate to allow of the detection of $\frac{1}{10000}$ part of creatinine (2) Weyl's test (Ber 1878, 11, 2175) consists in the production of a ruby-red colouration, changing to yellow when, to a solution of creatinine, a few drops of 10 p.c. sodium nitroprusside and the same quantity of 10 p.c. sodium hydroxide or carbonate solution are added On acidifying the solution with acetic acid and boiling, the colour becomes emerald green, changing to blue, due to the formation of Prussian blue (Salkowski; Colasanti, Gazz. chim. ital. 1887, 17, 129). Guareschi (Ber. 1888, 21, Ref. 372) has shown that this reaction is given by other compounds than creatinine containing the $—CO \cdot CH_2—$ complex. (3) Jaffé's test (Zeitsch. physiol. Chem. 1886, 10, 399) is the production of a deep-red colour, when picric acid and an excess of sodium hydroxide solution are added to the liquid containing the creatinine. Chapman (Chem. News, 1909, 100, 175) has shown that the colour is due to the sodium salts of amino-dinitrophenol (picramic acid), and diamino-nitrophenol formed by the reduction of the picric acid by the creatinine; if the creatinine is present in excess, reduction to the colourless triaminophenol occurs.

The older methods for the estimation of creatinine were based upon the isolation of the base in the form of its sparingly soluble double salt with mercuric or zinc chloride, and either weighing the precipitate or estimating the metal

or the nitrogen in the compound (Neubauer, Annalen, 119, 35; Salkowski, Zeitsch. physiol. Chem. 1886, 10, 113; Grocco, Chem. Zentr. 1887, 17; Kolisch, *ibid.* 1895, i. 814; Ladd and Bottenfield, Amer. Chem. J. 1898, 20, 869). Edleson (Chem. Zentr. 1909, i. 108) recommends precipitating the sulphate in the presence of alcohol and ether, dissolving it in water, and titrating the solution with standard barium hydroxide solution, using phenol phthalein as indicator.

The method generally adopted for estimating creatinine in urine is Folin's colorimetric method, based on Jaffé's reaction (Zeitsch. physiol. Chem. 1904, 41, 223). N/2 potassium dichromate solution is placed to a height of 8 mm. in one tube of a Duboscq colorimeter; 100 c.c. of the urine is placed in a 500 c c. flask with 10 c.c. of a 1 2 p.c. solution of picric acid and 5 c.c. of a 10 p.c. solution of sodium hydroxide, left for a few minutes and made up to the mark. If x is the length of this solution in the second tube required to give the same colour effect as the 8 mm. of the standard dichromate solution in the first tube, then $8 \cdot 1 \times 10/x = mg$. of creatinine in the 10 c c. of the urine. If x is less than 5, only 5 c c. of urine should be used; if x is greater than 13, then 20 c.c. of urine should be used. If creatine is also present in the urine, the amount may be estimated by first determining the creatinine as above, then converting the creatine in another 10 c.c of the urine to creatinine by heating it with 5 c c. of N/2 HCl on the water-bath for 3 hours or for 15 minutes at 117° under pressure (Benedict and Myers, Amer. J. Phys. 1907, 18, 362), or by boiling down to dryness with an equal volume of hydrochloric acid (Benedict, J. Biol. Chem 1914, 18, 191-194), and estimating the total creatinine. The difference between the two results represents the amount of creatinine equivalent to the creatine originally present. (For precautions to be observed regarding temperature, time, and dilution, in applying this method for the estimation of creatinine, compare Chapman, Chem. News, 1909, 100, 175.) Folin and Morris (J. Biol. Chem. 1914, 17, 469-473) recommend the use of a standard solution of creatinine instead of a dichromate solution; *see also* Folin and Doisy (*ibid.* 1917, 28, 349-356); Gettler (*ibid* 29, 47). The presence of dextrose, acetone and aceto-acetic acid interferes with the final colour reaction and various suggestions have been made for overcoming the difficulty (Graham and Poulton, Proc. Roy. Soc. 1914, B, 87, 212; Greenwald, J. Biol. Chem. 1913, 14, 87; Rose, J. Biol. Chem. 1912, 12, 73-80). Morris, J. Biol. Chem. 1915, 21, 201-208, recommends the preliminary precipitation of creatinine as the double potassium picrate. *See* Bauman and Ingvaldsen (*ibid.* 1916, 25, 196-200) for the quantitative precipitation of creatinine with potassium picrate.

An isomeride of creatinine, *alacreatinine*,

NH —— CO

HN : C

NH —— CHMe
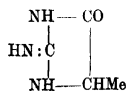
was prepared in 1873 (Ber. 6, 1371), and other isomerides have been described by Korndörfer, Arch. Pharm. 1904, 242, 620; Schenck,

ibid. 1910, 248, 376, and 1911, 249, 463; Schmidt, *ibid.* 1910, 248, 568; Johnson and Nicolet (J. Amer. Chem. Soc. 1915, 37, 11, 2417) obtained two methyl glycocyamidines isomeric with creatinine by the action of methylamine on the ethyl ester of benzoylpseudoethylthiohydantoic acid.

Two isomeric *nitrosocreatinines* were obtained by Dessaignes (Annalen, 1856, 97, 341) and Marcker (*ibid.* 1865, 133, 305) by passing the nitrous fumes from the action of nitric acid on arsenious oxide into an acid solution of creatinine The less soluble *α-nitrosocreatinine* $C_4H_8O_2N_4$ decomposes at 210°, forming a colourless liquid that quickly solidifies to a brown mass from which a new *base* $C_7H_{12}O_3N_{10}$ (?) can be extracted; it forms a crystalline *nitrate, hydrochloride,* and *platinichloride,* and yields the *bromoderivative* $C_4H_7O_2N_4Br$. The more soluble *β-nitrosocreatinine* $C_4H_8O_2N_4$ melts at 195° to a brown liquid and decomposes at 220°.

According to Kramm (Chem Zentr 1898, 1 37), the yellow colour formed by the interaction of sodium nitroprusside and sodium hydroxide on creatinine (*cf.* Weyl, Ber. 1878, 11, 2175), is due to the formation of a *nitrosocreatinine* $C_4H_6O_2N_4$, which can be isolated as a colourless crystalline precipitate by adding acetic acid to the yellow alkaline solution and shaking vigorously. According to Schmidt and Hennig (Arch. Pharm. 1912, 250, 345) this is an oxime, they find that on treatment with sodium nitrite in nitric acid solution creatinine yields a mixture of methyl hydantoin oxime, m p. 193° 194°, and creatinine oxime, which begins to discolour at 250° but does not melt.

The following *acyl-* and *alkyl-* derivatives of creatinine have been prepared : *Benzoylcreatinine* $C_{11}H_{11}O_2N_4$, pale yellow needles, m p. 187° (Urano, Beit Chem. Physiol. Path. 1907, 9, 183); *methyl, dimethyl* and *trimethyl creatinine* and *salts* (Korndorfer, Arch Pharm. 1904, 242, 641; Kunze, Arch. Pharm. 1910, 248, 578–93).

Methyl creatinine
$$HN : C \begin{matrix} NMe \cdot CH_2 \\ | \\ NMe \cdot CO \end{matrix}$$
gives an aurichloride, m.p. 170°–171°, and dimethyl creatinine gives an aurichloride, m. p. 128°–129°, and a platinichloride, m p. 177°–179°. According to Kunze the constitution of dimethyl-creatinine is
$$MeN : C \begin{matrix} NMe \cdot CH_2 \\ | \\ NMe - CO \end{matrix}$$
; it reacts as a

tertiary base; *ethylcreatinine*
$$C \begin{matrix} NH - CO \\ : NEt | \\ NMe - CH_2 \end{matrix}$$
(Neubauer, Annalen, 119, 50), *sec* Henzerling (Arch. Pharm. 1910, 248, 594 ; the *platinichloride* crystallises in monoclinic plates, m p. 197°–211°; *ethylcreatinine* hydriodide, m.p. 217°–219°; *diethylcreatinine* platinichloride 201°–202°); *methylamino-α-butyrocyamidine*
$$HN : C \begin{matrix} NMe \cdot CHEt \\ | \\ NH \cdot CO \end{matrix}$$
ethylamino-α-butyrocyamidine $HN : C \begin{matrix} NEt \cdot CHEt \\ | \\ NH \cdot CO \end{matrix}$
ethylaminopropionocyamidine $HN : C \begin{matrix} NEt \cdot CHMe \\ | \\ NH \cdot CO \end{matrix}$

ethylaminoacetocyamidine $HN : C \begin{matrix} NEt \cdot CH_2 \\ | \\ NH \cdot CO \end{matrix}$
methylaminoisovalerocyamidine
$$HN : C \begin{matrix} NMe \cdot CH \cdot CHMe_2 \\ | \\ NH \cdot CO \end{matrix}$$
α-aminocaprocyamidine $C \begin{matrix} NH \cdot CO \\ : NH | \\ NH \cdot CH \cdot [CH_2]_3 Me \end{matrix}$
(Duvilher, Compt. rend. 1882, 95, 456; 96, 1583; 97, 1486; 100, 916; 103, 211; 104, 1290).—For *Xantho-, Cruso-,* and *Amphi-creatinine* v. *Xanthocreatinine.* M. A. W.

CREOLIN. A disinfectant consisting of an emulsion of coal tar cresols with soap.

CREOSOFORM. A condensation product of formaldehyde and creosote. Used as an internal antiseptic.

CREOSOL *v.* CREOSOTE, WOOD TAR.

CREOSOTAL (*Creosote carbonate*) is a mixture of carbonates of the phenols present in wood creosote, of which the chief are guaiacol and cresol.

It is produced by heating creosote with a benzene solution of carbonyl chloride (phosgene) under pressure (Heyden, Eng Pat 19074, 1890), but is generally prepared by passing phosgene gas through a solution of beechwood creosote in caustic soda solution The carbonate separates as an oil, and is washed with dilute caustic soda and finally with water,

Creosotal is a viscid yellowish liquid, insoluble in water, but soluble in alcohol, chloroform, benzene, &c (Aufrecht, Pharm. Zeit. 1908, 53, 480). When it is boiled with caustic potash, the odour of creosote is evolved. It is quite odourless, tasteless, and non-irritant in its action upon the mucous membrane, and is therefore much used as a substitute for creosote in the treatment of bronchial affections and pneumonia, especially in children (Weber, Pharm. J. 68, 115; Toff, *ibid* 73, 414) The dose for adults is about 60 grams daily, and it is usually given in an emulsion (Haefelin, Pharm. Zeit. 49, 141).

CREOSOTE or **KREOSOTE** (from κρέως, contracted genitive of κρέας, meat, and σωζώ, I save or preserve). Wood tar, and coal tar, when subjected to distillation, yield fractions technically known as ' creosote,' both of which, the latter more especially, find extensive and important uses in the industrial arts.

Reichenbach, in the year 1832, applied the term ' kreosote ' to a substance derived from wood tar, and which has been found to possess powerful antiseptic properties; shortly afterwards, Runge discovered carbolic acid in coal tar, and the two products were, for a considerable time, regarded as identical; similar compounds, however, have since been procured from other sources, and in order to prevent confusion, it has been suggested to restrict the use of the term 'creosote' to the use in a generic sense as referring to all the phenols and phenoloid bodies derived indifferently from coal, wood, coke-oven, blast-furnace, and shale-oil tars. The enormous extension of the use of creosote oil from coal tar for the preservation of timber has resulted in the terms 'creosote' and 'creosote oil' being used commercially as meaning the

heavier distillates from coal tar and coke oven-tar, the oils from blast-furnace tar being distinguished as 'blast-furnace creosote.'

Wood-tar creosote. The tar derived from the distillation of beechwood, when subjected to further distillation, yields certain fractions that are heavier than water, and which, after agitation with solution of caustic soda, and separation from insoluble oils, are boiled with free access of air in order to oxidise various impurities present; the alkaline solution thus obtained is decomposed with dilute sulphuric acid, the crude creosote which separates is again submitted to a similar alkaline and acid treatment, and the product finally distilled, reserving the fraction passing over between 200° and 220°.

This represents the ordinary 'wood-tar creosote' of commerce. It is a complex mixture of phenoloid compounds, the proportions of which are materially influenced by the method originally followed in distilling the beechwood from which it was obtained.

Wood-tar creosote, when freshly prepared, is a colourless, transparent liquid of an oily consistency, and which retains its fluidity at a very low temperature; its sp gr. varies from 1·037 to 1·087; it boils at 205°-225°, and dissolves in about 200 parts of water; its odour is strong and penetrating, resembling that of wood smoke, or rather of smoked meat; it refracts light powerfully and burns with a very sooty flame. Wood-tar creosote is powerfully antiseptic, but its power of coagulating albumen has been denied; nevertheless, it preserves animal substances as effectively as carbolic acid. It is less caustic than carbolic acid, and is not poisonous. Wood-tar creosote may be regarded as consisting of a mixture of compounds included in several homologous series, chiefly of acid methylic ethers of catechol, and the presence of the following bodies has been established:—

Name	Formula	Boiling point
1. Monohydric phenols ·		
Phenol, carbolic acid	C_6H_5OH	182°
Cresols, cresylic acid (1-2, 1-3, 1-4)	$\{C_6H_4(CH_3)OH$	203°
Xylenols or phlorols (1-3-4, 1 3 5)	$\}C_6H_3(CH_3)_2OH$	220°
Ethyl phenol (1-2)	$C_6H_4(C_2H_5)OH$	203°
2. Methyl ethers of dihydric phenols		
Guaiacol or methyl-catechol	$\{C_6H_4\{{OCH_3 \atop OH}$	200°
Creosol or methyl-homocatechol	$\{C_6H_3(CH_3)\{{OCH_3 \atop OH}$	219°
Dimethyl-homocatechol	$\}C_6H_3(CH)(OCH_3)_2$	214°–128°
Homocreosol or di-methyl guaiacol	$\{C_6H_2(CH_3)_2\{{OCH_3 \atop OH}$	230°
Ethyl-guaiacol(1-3-4)	$C_6H_3(C_2H_5)\{{OCH_3 \atop OH}$	—
Cœrullgnol or pro-pyl-guaiacol	$\{C_6H_3(C_3H_7)\{{OCH_3 \atop OH}$	241°
3. Methyl ethers of trihydric phenols:		
Dimethyl-pyrogallol	$C_6H_3\{{OCH_3 \atop {OCH_3 \atop OH}}$	253°
Dimethyl - methyl-pyrogallol	$C_6H_2(CH_3)\{{OCH_3 \atop {OCH_3 \atop OH}}$	265°
Dimethyl - propyl-pyrogallol (picamar)	$C_6H_2(C_3H_7)\{{OCH_3 \atop {OCH_3 \atop OH}}$	285°
Methyl-propyl-pyro-gallol	$C_6H_2(C_3H_7)\{{OCH_3 \atop {O \atop OH}}$	290°

Of these compounds, phenol is present in extremely small quantity, paracreosol in larger,

and phlorol in notable proportion, but the two principal constituents of creosote are guaiacol and creosol, although not equally present in all varieties; guaiacol, according to Allen, predominates in Rhenish creosote, whilst with Morson's creosote from 'Stockholm tar,' creosol is the chief constituent. Homocreosol and cœrulignol are present in small quantity only, but, according to Gratzel, the latter body possesses such energetic and astringent qualities that a single drop placed on the tongue causes bleeding; purified creosote should therefore be absolutely free from this compound, which may be detected by the blue colouration produced by barium hydroxide.

The less valuable portions of wood-tar creosote were found by A W. Hofmann to contain the methyl ethers of pyrogallol and its homologues; these bodies are of interest from the remarkable colouring matters (originally discovered by Runge) which may be derived from them by oxidation; thus, if the sodium derivative of dimethyl-pyrogallol be mixed with the sodium derivative of dimethyl-methyl-pyrogallol and excess of sodium hydroxide and heated in the air, a substance called *eupittonic acid* is formed, according to the following equation:—

$$(C_8H_{10}O_3)_2 + C_9H_{12}O_2 + 2O_2 = C_{25}H_{26}O_9 + 3H_2O$$
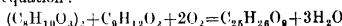
Eupittonic acid has the constitution of a hexamethoxyl aurin $C_{19}H_8(OCH_3)_6O_3$. Reichenbach's 'pittical,' called by Wichelhaus 'eupittone,' was a salt of eupittonic acid. Wood-tar creosote has been met with adulterated to a considerable extent with crude carbolic and cresylic acids, and from the fact that the reactions of these substances closely resemble those of wood creosote, the distinction between the two, especially when in admixture, is attended with some difficulty. Genuine beechwood tar is soluble in solutions of caustic alkalis, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide; on the other hand, it is practically insoluble in strong ammonia.

An alcoholic solution should give no colouration whatever (blue or red) with baryta water; such colouring indicates the presence of cœrulignol and other impurities.

The composition of beechwood and oak creosotes, freed from hydrocarbons, is given by Béhal and Choay (Compt. rend. 1894, 119, 166), as follows:—

	Beech	Beech	Oak
Distillation temperature, °C.	200–220°	200–210°	200–210°
Specific gravity	1·085	1·085	1·068
Monophenols	39·0	39·0	55·0
Guaiacol	19·7	26·5	14·0
Creosols and homologues	40·0	32·1	31·0
Loss	1·3	2·4	—

Owing to the demand for guaiacol for pharmaceutical purposes, wood-tar creosote, as it occurs in commerce, is frequently found to have been deprived of part or the whole of the guaiacol it contained.

Methods for the determination of guaiacol in wood creosote are given by Béhal and Choay (Compt. rend. 1893, 116, 197); M. Adrian (Nouv. Rem. 13, 97); L. F. Kebler (Amer. J. Pharm. 1899, 409).

Wood-tar creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerol; it is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose; shaken with half its volume of collodion, B.P., Calvert's No. 5 carbolic acid coagulates the gun-cotton. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution; when a mixture of equal volumes of Morson's creosote and Calvert's No. 5 acid is treated with the collodion, the precipitation is very marked.

Creosote from coal tar and other sources. In pharmaceutical circles the term 'creosote' is still retained for products of the carbonisation of wood, but, generally speaking, it is recognised in industry as applying to a mixture, consisting principally of hydrocarbons distilled from coal tar, the latter being either of gasworks origin, or from the carbonisation of coal in coke ovens. At the time when anthracene was a valuable commercial product, the fraction of coal tar containing this material was usually collected separately, the crude anthracene being removed by filtration, and the oil separated therefrom being placed on the market under the names 'anthracene oil,' 'green oil,' or 'heavy oil.' In more recent times many tar distillers have found the recovery of naphthalene unremunerative, and this is especially the case where the crude tar is of such a nature that an appreciable proportion of solid paraffinoid hydrocarbons appears. The whole of the anthracene fraction has therefore frequently found its way to the creosote storage. Other distillates of coal tar have also been passed into the creosote tanks at various works, including the 'sharp oil' separated during the recovery of crude naphthalene, and the 'middle oils' or 'carbolic oils,' after treatment for the removal of 'tar acids' (crude phenols). There is no very serious objection to this development, especially in view of the fact that inclusion of the anthracene fraction results in a mixture containing a large proportion of high-boiling constituents. Creosote of this nature is employed in the United States for railway work, and has been exported in recent times to that country in very large quantities by means of 'tankers.' But exception must be taken to the practice that has arisen in some cases whereby the creosote storage has largely assumed the character of a refuse pit for the disposal of various oils, and even tars, that are only marketable with difficulty, such as blast-furnace tar, blast-furnace creosote, water-gas tar, &c. It is probably most satisfactory to regard creosote as a fraction obtained during the distillation of coal tar, either of gasworks or coke-oven origin, collected between the light oil fraction and the anthracene fraction; it may or may not include the middle oils, or those portions of them remaining after partial or complete removal of tar acids or naphthalene.

Creosote from coal tar (gasworks). This consists, for the most part, of a mixture of liquid aromatic hydrocarbons with naphthalene.

The naphthalene may be present in such small quantities that the oils retain it entirely in solution, or there may be so much of it, say up to 40 p.c., or more, that the creosote exists as a solid mass at 15° C. Phenolic and basic constituents are also present, together with small amounts of paraffinoid hydrocarbons. The creosote produced from tar that is made in London and the southern districts of England, where Durham and other north country coals are largely carbonised, contains considerably more naphthalene, as a rule, than that obtained in more northerly districts, where Midland coals are retorted. On the other hand, the creosote obtained from Midland tar is far richer in tar acids than that made in London. So characteristic are these features that various creosotes are regularly known in the trade as 'Midland creosote,' 'ordinary London creosote,' &c. Scotch creosote will be dealt with later. The carbonisation of coal in gasworks has, during the last few years, developed in several directions. It was formerly the custom to work with 'light charges' of coal in the retorts, with the result that a relatively large free-space existed between the surface of the coal and the top of the retort. But about 1911 the practice was widely adopted of employing heavier charges, whereby the 'free space' was greatly reduced. The result of this change of procedure was that the volatile products of carbonisation experienced a much more rapid journey to the ascension pipes of the retort, and consequently the changes they underwent, due to thermal decomposition in the free space, were lessened. The effect of this change on the quality of the tar was very noticeable. The quality of the creosote seems to be very similar to that resulting from 'light charge' carbonisation, but there is more of it in the tar. The proportion of naphthalene in the creosote is lower, while the proportion of tar-acids is somewhat higher. The average yield of creosote from coal tar is roughly about 20 p.c. of the latter by volume.

Creosote being a mixture of many hydrocarbons, &c., it is not possible to give any definite figures for its physical and other constants, and the more so as it is highly improbable that any two makes are identical. When a sample of good quality is distilled in the laboratory, the main bulk of it usually passes over between 200° and 300° C., the bulb of the thermometer being immersed in the vapour. If the anthracene fraction be present there will be a considerable residue at the latter temperature. The calorific value is about 16,050 B.Th.U. The evaporating power (in actual practice, 'from and at 212° F.') is 12·0 lbs. The flash-point usually lies about 170°–180° F. (closed test). The refractive index of the higher fractions should be above 1·6 (Sage). Determination of the specific heat between 30° and 100° C. gave the figure 0·398. The co-efficient of expansion per °F. is about 0·000455. The specific gravity usually lies between 1·030 and 1·080. Creosote generally contains between 0·5 and 0·9 p.c. of sulphur.

Although these figures naturally differ with the various makes of creosote, and can therefore only be regarded as approximate, they, nevertheless, are frequently found useful in industry, and several serve as evidence of admixture of

adulterants of a paraffinoid nature, such as have already been mentioned in this article.

Creosote finds its largest application in the treatment of wood, especially railway sleepers, piles, and telegraph poles. Its employment as fuel is being very rapidly developed, chiefly in burners which serve to atomise the liquid, either by direct application of pressure, or by means of steam or air under pressure. Numerous patents have been granted for such burners, and for further information on the subject, consultation of such works as Brame's Fuel may be recommended. The employment of creosote as a fuel for Diesel engines, with or without pilot ignition, is extending, and the 'Diesel Engine Users Association' has recently issued a specification for the quality of oil considered to be best suited for that particular purpose. Creosote oil is (when freed from naphthalene) used in the preparation of disinfectants and sheep-dips. It is also employed for generating artificial light in specially designed lamps such as the 'Lucigen.'

Lamp-black is manufactured by partial combustion of creosote in a limited air supply. Recent experiments seem to indicate the possible value of creosote as a soil steriliser.

The best known methods of creosoting timber are perhaps those of Bethel, Boulton, Rüping, Curtis Isaacs, Lawry, Rutgers. In some of these processes the creosote is applied under pressure, occasionally after first placing the timber under a vacuum, and at other times the oil is employed at a temperature sufficiently high to boil the sap out of the wood *in vacuô.*

Many specifications for creosote considered to be best suited for this work have been published; probably the best known is that of Dr. Tidy. The advantages resulting from the creosoting of timber are summarised by Tidy as follows:—

Physical.—Choking of pores, and thus rendering the material non-absorbent of water.

Biochemical.—Inhibition of germ life.

Chemical.—Coagulation of albumen by the tar acids.

Probably most of the creosote sold for creosoting at the present time is subject to the American 'Maintenance of Way' specification. The most important feature is the insistence on a large proportion of high-boiling oils. It is estimated that in 1913, 35,000,000 gallons of creosote were exported to the United States from the United Kingdom. At various times emphasis has been given to one or more of the following properties of creosote for treatment of timber :

1. Maximum naphthalene content.
2. Minimum naphthalene content.
3. Tar acids.
4. Proportion of high-boiling constituents.

It is considered that the life of railway sleepers is increased five-fold by creosoting. Experiments by J. M. Weiss (U.S.A.) (*see* J. Soc. Chem. Ind. 1911, 1348), show that coal tar creosote is more efficient as a preservative than is that from water-gas tar, in the proportion of about 6 to 1. Creosote is used for the treatment of wooden paving blocks, for which purpose it is valuable both with phenoloid compounds, and also as a means of rendering the blocks impervious to

water, the absorption of which would give rise to expansion of the wood.

The following are among the tests commonly applied to creosote :—

1. Distillation.
2. Liquidity of residue left after distillation.
3. Water.
4. Solid matter (naphthalene, &c.) deposited at 60° F.
5. Loss on evaporation under specified conditions.
6. 'Absorbent spot '—a drop of the oil being placed on blotting-paper, and examination made for particles of ' free carbon ' indicative of adulteration by crude tars.
7. Tar acids.
8. Specific gravity.
9. Colour.
10. Fluorescence.
11. Refractive index—serving to indicate presence or absence of paraffinoid hydrocarbons, or tars containing them.
12. Flash point.
13. Matter insoluble in benzol.
14. Sulphonation.

(*Cf.* Sage, J. Soc. Chem. Ind. 1911, 588.)

Creosote from coke-oven tar is very similar to that from gasworks tar.

Oils from low-temperature processes of carbonisation. A great deal of work has been carried out in investigating the products of these systems. Some of the processes are worked under partial vacuum. The volatile products of carbonisation are not subjected to the secondary thermal decompositions that are incidental to high-temperature work in horizontal retorts, with the result that the proportion of aromatic hydrocarbons appearing in the oils is very much smaller, the specific gravity of those fractions corresponding to creosote being lower than 1·000. The content of tar acids is very much higher, though there is but little actual phenol. From the highest fractions solid paraffinoid hydrocarbons are frequently deposited. Work by Pictet and Bouvier, on the carbonisation of coal at low temperatures and in partial vacuum, points to the conclusion that the primary condensible products are similar to the constituents of certain petroleums, consisting to a considerable extent of terpenes and naphthenes. No solid aromatic hydrocarbons are present. On subjecting these low-temperature tars to heat by passage through a tube or over red-hot coke, benzene, naphthalene, anthracene, &c., are formed, the resulting oils being very similar to ordinary coal tar creosote. According to Wheeler, 'vacuum' tar is largely a mixture of ethylenic, naphthenic and paraffin hydrocarbons, and homologues of naphthalene, together with phenoloid compounds, chiefly cresols and xylenols. Aromatic solid hydrocarbons are generally absent. D. Trevor Jones concludes that the ordinary products of coal tar result from the action of heat on a tar which is formed in the first instance, and which is similar to that obtained under low-temperature conditions. The naphthenes, paraffins and unsaturated hydrocarbons are decomposed to produce olefines, which are at their maximum at 550° C. The olefines vanish at 750° with the simultaneous appearance of naphthalene and of large quantities of hydrogen. He further

concludes that acetylene plays an insignificant part in the formation of coal tar products. Low temperature carbonisation on the large scale yields a very oily tar amounting to 25 or more gallons per ton of coal. This tar is rich in those oils corresponding in distilling range to the creosote of normal tar. In the carbonisation of cannel coal by such processes as much as 50 gallons of tar is obtained.

Creosote from vertical retort tar is characterised by its low content of naphthalene, its high content of tar acids (chiefly higher homologues of phenol), and the large proportion of paraffinoid bodies present, the latter being sufficient to bring the specific gravity below 1·000.

West introduces steam during the process of vertical carbonisation, using continuous vertical retorts The yield of tar is increased very considerably and reaches 20 gallons per ton. The tar is of low specific gravity and gives a large ' creosote' fraction. The tars evolved during the carbonisation of coal in vertical retorts are not subject to such high temperatures as in the case of horizontal retorts. Consequently these tars resemble, to a certain extent, the low-temperature products already described. Similar remarks apply to the tars from blast furnaces and from power-gas producers, where coal is employed as fuel.

Blast furnace creosote. This is sometimes known as ' phenoloid.' It resembles vertical retort creosote in many ways. The specific gravity of the hydrocarbons is low, the proportion of tar acids is high, reaching 20–35 p.c., though there is little phenol. The phenoloids from blast-furnace tar, extracted by Watson Smith, contained only 1·33 p.c of real phenol, boiling at 182°, whereas the tar acids from Lancashire tars yielded 65 p.c. of crystallisable carbolic acid.

The fractions passing over between 210° and 230° contain phlorol and creosol, and those following at a higher temperature, viz 360°, furnish compounds allied to the cupittonic acid obtained from wood tar.

This creosote has a very strong and characteristic odour. Blast furnace creosote, which is sometimes even the crude tar from which it is distilled, is often mixed with coal tar creosote, and several of the tests generally applied to the latter are employed for the purpose of detecting this undesirable adulterant.

Blast-furnace creosote oil is now produced in large quantities in Scotland. It is employed to a certain extent for creosoting timber, in producing the ' Lucigen' light, and as a liquid fuel. It furnishes from 20 to 35 p.c. of phenoloid substances soluble in caustic soda, as against 4 to 7 p.c. in London coal-tar creosote, and about 16 p.c. for Midland and country make. Allen and Angus have secured by patent their use as an antiseptic under the name of ' neosote,' a word signifying ' new preserver' (Eng. Pat. 11689, August 29, 1887). Experiments have shown that the substance compares favourably with carbolic acid, whilst its caustic properties, when applied to the skin, are much less marked. When freshly prepared, the fluid is almost colourless, and bears a great resemblance to wood-tar creosote.

Creosote from producer tar. In cases where

bituminous coal is gasified a tar is formed, the creosote from which is similar in several respects to the blast-furnace oil. Tar acids and paraffinoids are present in large quantity.

Creosote from water-gas tar is characterised by the absence of tar acids. It is usually rich in paraffins, of low specific gravity, and may contain anthracene and naphthalene.

Scotch creosote is characterised by its large content of paraffinoid hydrocarbons and consequent low specific gravity.

Employment of creosote oils for lighting.— Creosote oil has long been employed as a source of light in the construction of harbours and outdoor work, where smoke was of little consequence or inconvenience ; but when it is wished to burn this oil to the greatest advantage and with the least possible amount of smoke and soot, it becomes necessary to employ lamps so constructed that a jet of air or steam, more or less superheated, may be introduced in such a manner as to ensure more perfect combustion. Hartmann and Lucke (D. R. P. 9195, Aug. 9, 1879) constructed a lamp specially intended for the consumption of creosote oils, in which the oil is automatically supplied to a dish-shaped receptacle, over which is placed a funnel-shaped cylinder. In the centre of the dish or receptacle receiving the oil from its attached reservoir, is placed a conical tube, reaching a little above the surface of the oil, and through which a jet of superheated or dry steam may be driven. In using the lamp, the dish or receptacle referred to is allowed to fill with oil ; it is then ignited at its surface, the funnel-shaped cylinder placed over it, and steam cautiously admitted through the conical tube. It will readily be seen that the arrangement closely resembles the ' Herapath blowpipe,' with the difference that the steam is forced through a body of combustible fluid, issuing just above its surface, in place of air forced through a body or envelope of combustible gas, and issuing at a point or position that may be called its surface.

The oil thus burns without wick or chimney, and affords a light of 180 standard candles, with an hourly consumption of a little over 2 lbs. of creosote.

An apparatus for a similar purpose has been patented by Lyle and Hannay, under the name of the ' Lucigen.' It consists of an oil tank or reservoir, fitted with a special burner at the top of a tube, which may be extended to any length ; into this reservoir compressed air is introduced by an indiarubber pipe, so attached as to make the ' Lucigen' portable. On the compressed air being admitted into the oil tank or receptacle, it forces the oil up through an internal tube, and, escaping at the same time with the oil in the burner, produces a spray which is set on fire. A light of about 2000 candle-power is given by the ' Lucigen.' The flame is large, the light well diffused, and the eyes are not dazzled by it. There is little or no smoke from the flame, and the lamp burns equally well under heavy rain or spray ; it requires no lantern, and has no parts which can be damaged by rough usage. In the ' Doty' and ' Wells' lights, pressure is brought to bear on the surface of the oil or creosote by means of an air pump, whereby the oil is forced through a coil surrounding the lower portion of the flame, and becomes distilled into gas.

Creosote oil has also been employed for the purpose of illuminating and heating, by direct conversion into permanent gas. A ton of creosote is capable of yielding 13,300 cubic feet of gas, with an illuminating power of 14 candles ; a yield of 29,300 cubic feet may be obtained, but of 8½ candle-power only ; the chief drawback to this method of utilisation is the high temperature necessary to decompose the oils, which results in the production of low candle-power gases.

Employment of creosote as fuel.—Creosote oil is extensively used as a fuel, both for marine and stationary purposes and especially. for furnaces for heating iron rods for the manufacture of bolts and rivets. From theoretical considerations, it would appear to be eminently adapted to the purpose, 1 lb. of coal-tar creosote, when effectively burnt, being capable of evaporating 11·24 lbs. of water, a result which is considerably in excess of that obtained from coal or coke.

Various methods have been devised for burning the oil to the greatest advantage. These may be briefly summarised under the following heads :—

1. Injection into the furnace by means of compressed air with ' atomising ' apparatus.

2. Injection into the furnace by means of steam with ' atomising ' apparatus.

3. Feeding into the furnace by simple gravitation, alone or in combination with coke.

G. F. Dexter (Journ. Gas Lighting, June 29, 1886, 1242-1244), in a table showing the relative calorific values of certain coal-tar distillates, refers to creosote, or heavy oils, as under :

Average formula $C_{14}H_{16}$; b p. 240° to 270° and upwards.

Proportionate weight of constituents :

| Carbon | . | . | . | 0·93913 |
| Hydrogen | . | . | . | 0·06087 |

Calorific value :

| Carbon units | . | . | . | 497 |
| Hydrogen units | . | . | . | 210 |

Employment of creosote oil as an antiseptic and for the purposes of a cattle wash and sheep dip (v. DISINFECTANTS).

Creosote oil is also now largely used to absorb benzene from coke-oven gas. The gas, after the extraction of the ammonia, is passed up towers or scrubbers down which a shower of creosote oil falls. The creosote oil takes up from 3 to 4 p.c. of benzene, and this is regained by distillation with steam, the creosote being used over and over again until, by the accumulation of dirt and tar, it becomes too viscid, when it is generally run into the tar well. This fact should not be lost sight of when estimating the proportion of creosote in coke-oven tars.

The heavier portions of creosote oil are also used to absorb naphthalene from coal gas : the gas is passed through washers containing the oil. As the oil tends to abstract some of the illuminants from the gas, it is best to add to the oil before use a small proportion of benzene sufficient to saturate the oil so that no more is absorbed from the gas.

The heavier oils are also used as a rough lubricant for brick-making machinery, and for

injecting into the brick kilns during the burning of the bricks to impart a superficial blue colour to them. The creosote acts as a reducing agent on the iron compounds in the clay, and the red colour is changed to blue.

A preparation of heavy creosote or anthracene oil with lime is used as a cart or axle grease.

Bibliography.—Lunge's Coal Tar and Ammonia ; Allen's Commercial Organic Analysis ; Warne's Coal Tar Distillation. W. H. C.

CREOSOTAL. Syn. for Creosol carbonate.

CRESATIN. Acetic ester of *m*-cresol.

CRESEGOL. Trade name for the mercury-potassium salt of cresol sulphonic acid.

CRESOL $C_6H_4(CH_3)OH$. The three isomeric cresols exist in coal tar (Williamson and Fairlie, Annalen, 92, 319 ; Ihle, J. pr. Chem. [2] 14, 442 ; Tiemann and Schotten, Ber. 11, 767, 783) in about the following proportions : orthocresol, 35 p.c. ; metacresol, 40 p.c. ; and paracresol, 25 p.c. (Schulze, *ibid.* 20, 410).

The cresols can be separated from the oily, non-crystallisable mother liquors obtained in the purification of crude phenol by fractionation and crystallisation, by dissolving them in soda lye, freeing the solution from naphthalene or other hydrocarbons by a current of steam, and then fractionally precipitating with sulphuric acid. The first fractions, owing to the greater acidity of phenol, contain chiefly cresols, and are further purified by distillation (Müller, Zeitsch. Chem. 1865, 270).

Various processes have been patented for obtaining meta- and para-cresol from crude cresol Raschig (Eng. Pat. 18334 ; D. R. P. 112545 ; J. Soc. Chem. Ind. 1900, 37), by repeated fractionation of the crude cresol, obtains a mixture containing 60 p.c. of meta- and 40 p.c. of para-cresol. This mixture is then sulphonated by means of concentrated sulphuric acid, in which *m*-cresolsulphonic acid is easily soluble, but the *p*- compound only with great difficulty. The mixture is allowed to stand for a week, and the crystals of the *p*-sulphonic acid are removed, or a soluble sodium salt, such as the sulphate, may be added in quantity sufficient to form the sodium salt of the *p*-cresolsulphonic acid. The latter is separated from the mother liquor, which consists of *m*-cresolsulphonic acid and a little sodium sulphate. The two cresols are obtained from their respective sulphonic acids by hydrolysis with superheated steam. In another process (Raschig, Eng. Pat. 25269 ; J. Soc. Chem. Ind. 1900, 1099) the mixture of the two sulphonic acids is subjected to the action of superheated steam at 120°-130°, the *m*-cresolsulphonic acid alone being hydrolysed under these conditions. The *m*-cresol distils off, and on raising the temperature to 140°-160°, the *p*-sulphonic acid is hydrolysed and *p*-cresol is obtained. *See also* Raschig, D. R. PP. 144903, 146752.

According to the Chem. Fabr. Ladenburg (D. R. P. 148703 ; Chem. Soc. Abstr. 1904, i. 312), separation of *m*- and *p*-cresols, by partial sulphonation, is incomplete. The process recommended is to heat crude cresol with sodium hydrogen sulphate at 100°-110°, dissolve the product in water, when *p*-cresol separates out as an oily layer, the *m*-cresol alone being sulphonated. Superheated steam, at 180°, is

passed in to obtain *m*-cresol, after the *p*-cresol has been separated.

Another process of the same firm (Eng. Pat. 1881; Fr. Pat. 339880; D. R. P. 152652; J. Soc. Chem. Ind. 1904, 759) consists in saturating the crude cresol with milk of lime, when the calcium salt of *m*-cresol, which is much less soluble than that of the *p*-cresol, separates out. This is filtered off, decomposed with acid, and relatively pure *m*-cresol is obtained. The crystals of the calcium salt, before decomposition with acid, may be washed with benzene to free them from the last traces of mother liquor. Reihm (D. R. P. 53307; Frdl. ii. 9) separates *m*-cresol from *p*-cresol by means of their barium salts.

Rütgers (Fr. Pat. 317512; D. R. P. 137584 and 141421; J. Soc. Chem. Ind 1902, 1410) treats the commercial mixture with anhydrous oxalic acid or an anhydrous acid oxalate. By this means, the oxalic ester of *p*-cresol alone is formed and separates out. This ester is separated and decomposed by water into *p*-cresol and oxalic acid; the *m*-cresol is obtained from the mother liquors.

Terrisse (D. R. P. 281054) sulphonates the mixture with acid of 60° Bé, at diminished pressure, neutralises with sodium carbonate and drives off the *p*-cresol in a current of steam. The residual sodium salts are decomposed by sulphuric acid and the *m*-sulphonic acid then heated with superheated steam; *see also* Hoffmann Laroche and Co., Fr Pat. 454534.

Synthetical preparation of ortho- and para-cresol.—Pure ortho- and para-cresol can be obtained by fusing the potassium salts of the corresponding toluenesulphonic acids with alkali (Engelhardt and Latschinow, Zeitsch. Chem. 1869, 620), or by diazotising the corresponding toluidines. For this purpose the toluidine (15 parts) is dissolved in sulphuric acid of sp gr. 1·8 (15 parts) diluted with 500 parts of water, treated with an aqueous solution of potassium nitrite (12 parts), and the product gradually heated with steam. The resulting cresol is then distilled with steam, the distillate treated with soda lye, then with sulphuric acid, and the liberated cresol extracted with ether and finally distilled in a current of carbon dioxide (Tiemann and Schrotter; Ihle (*loc. cit.*)).

Orthocresol can also be obtained from carvacrol by treatment with phosphorus pentoxide (Kekulé, Ber. 7, 1006). It is crystalline, sp.gr. 1·0512 at 15·5°, melts at 30° (T. and S.; Ihle; Béhal and Choay, Compt. rend. 118, 1211); boils at 188·5° (B. and C.), 188° (T. and S.) at 191° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1182; Fox and Barker 191·8°), is soluble to the extent of 2·5 vols. in 100 vols. of water, and on fusion with caustic potash is converted into salicylic acid. When nitrated, it yields dinitroorthocresol (m.p. 86°-87°) (Nölting and Salis, Ber. 14, 987). Refractive index at 40° (μ_D) 1·53719.

Metacresol is prepared by heating thymol (100 parts) with half its weight of phosphorus pentoxide for 10–12 hours until propylene ceases to be evolved, adding the product to 115–120 parts of fused alkali, and further heating the fused mixture for 5–10 minutes to decompose the cresyl phosphate formed. The fused mass is then dissolved in water, treated with ether to

remove any undecomposed cresyl phosphate and other impurities, acidified with hydrochloric acid, and the separated metacresol extracted with ether, and finally distilled in a current of carbon dioxide (E. and L.; T. and S.).

Metacresol is also prepared from naphthalene 1.3.3´-, 1.3.6-, or 1.3.8- trisulphonic acids, from analogous hydroxy- or amino-naphthalene mono- or di-sulphonic acids or from trihydroxynaphthalene; *e.g.*1.3.3´- naphthalene trisulphonic acid together with half its weight of caustic soda and three-quarters of water, is heated for 5 hours at 280°. The product is poured into water, acidified, boiled to expel sulphurous acid, and filtered : *m*-cresol separates out on cooling (Kalle & Co. Eng. Pat. 16559; D R P. 81484; J. Soc. Chem. Ind. 1895, 1800; Hoffmann La Roche and Co. D. R. P. 247272). It is ordinarily a liquid of sp.gr. 1·0387 at 15·5°, but can be obtained in crystals, melting at 2·4° (Fox and Barker); it boils at 202° (corr.) (P.); and is soluble to the extent of 0 53 vol. in 100 vols. of water. Its aqueous solution is coloured blue by ferric chloride. When fused with caustic potash, it is converted into metahydroxybenzoic acid, and on nitration it yields a trinitro- derivative (m p. 105°-106°) (Nolting and Salis, Ber. 14, 987; 15, 1858). Refractive index at 40° (μ_D) 1·53322.

Paracresol crystallises in prisms, melts at 36° (Barth, Annalen, 154, 358 [B. and C.]), 36°-37° (T. and S.), and boils at 198° (I.), at 198°-199° (T. and S , B and C.), at 202° (corr.) (P.); and is soluble to the extent of 1·8 vols. in 100 vols. of water. Its aqueous solution gives a blue colour with ferric chloride. When fused with caustic potash, it is converted into parahydroxybenzoic acid, and on nitration it yields a dinitro- derivative (m p. 85°) (Richter, Annalen, 230, 313; Nolting and Salis, *l.c.*).

The crude cresol, as obtained from coal tar, is only slightly soluble in water, but its solubility in an aqueous solution of potassium cresol, renders its employment as an antiseptic possible. This solution is named *solveol* (Lacroix-Hunkiabéyendian, J. Pharm. Chim. 28, 34). The crude cresol is also frequently mixed with soaps, and is used in that form for disinfecting purposes (Dammann, D. R. P. 52129; Frdl. ii. 538; Holmers, D. R. P. 76133 and 80260; Frdl. iv. 1119 and 1120; Raschig, D. R. P. 87275; Frdl. iv. 1121; Engler and Dieckhoff, Arch. Pharm. 230, 561; 232, 351).

Oxidation with peroxides at a high temperature converts the cresols into the corresponding hydroxybenzoic acids (Friedländer and Löw-Beer, D. R. P. 170230; J. Soc. Chem. Ind. 1907, 434).

A mixture of nitro- derivatives, obtained by sulphonating coal-tar cresol and nitrating the sodium salt of the resulting cresolsulphonic acid with nitric acid of sp.gr. 1·2, has been employed, under the names 'Victoria yellow,' 'saffron surrogate,' as a dye for wool and silk; and, although poisonous (compare Weyl, Ber. 20, 2835; 21, 512), has been used as a colouring matter for butter, cheese, &c. By heating crude cresol with sulphur and alkali sulphide, or with alkalipolysulphides, or with a mixture of sulphur and alkalis, at a high temperature, brown sulphur compounds are obtained which are used for dyeing cotton (Farb. vorm.

F. Bayer & Co., D. R. P. 102897 ; Chem. Zentr. 1899, ii. 352).

CRESOLIN. A disinfectant composed of crude phenol and rosin soap.

CRESOLINE YELLOW v. AZO- COLOURING MATTERS.

CRESORCINOL v. PHENOL AND ITS HOMOLOGUES.

CRESOSTERIL. Acid-o-oxalic ester of m-cresol.

CRESOTIC ACID $CH_3\diagdown\ \diagup$ $\begin{matrix}OH\ CO_2H\end{matrix}$. A homologue of salicylic acid and obtained from o-cresol by similar methods to those employed in preparing salicylic acid from phenol; m.p. 163°–164°.

CRESYLIC ACID. The non-crystallisable, higher boiling portion of the phenols obtained in the purification of phenol (q.v.) is, after redistillation, known commercially as cresylic acid or liquid carbolic acid. It is a colourless, oily, refractive liquid, does not solidify at −80°, has a sp gr. 1 044, and consists of 40 p.c. metacresol, 35 p.c. orthocresol, and 25 p.c. paracresol (Schulze, Ber. 1887, 410). It is much less soluble than carbolic acid in water, ammonia, glycerol, or caustic soda, but more readily so in petroleum spirit. It boils at a higher temperature (about 185°–203°), gives a mixture of m-tribromo and o- and p-dibromo derivatives with bromine. It is even more readily acted upon by concentrated sulphuric and nitric acids than carbolic acid (Lunge, Coal Tar and Ammonia, ed. 1900, 182 ; v. also Allen, J. Soc. Chem. Ind. 1890, 141). Its antiseptic properties are more marked than those of carbolic acid or of either of the three cresols. Cf. CRESOL.

For a method of estimating phenol in commercial cresylic acid, see Fox and Barker (J. Soc. Chem. Ind. 1917, 842 ; 1918, 265 T.

CRESYL BLUE v. OXAZINE COLOURING MATTERS.

CRETAFORM. Oxymethyl cresol tannin.

CRISTOBALITE. A native form of silica (SiO_2) crystallising in the cubic system (pseudocubic). It was first recognised by G. vom Rath in 1886 as regular octahedra up to 2 mm. across, associated with tridymite, in cavities in andesite from the Cerro de San Cristóbal, near Pachuca in Mexico. It has since been found in volcanic rocks in the Rhenish district, Central France, and California, and in certain meteorites. The milk-white, translucent crystals are twinned and exhibit optical anomalies ; these disappear suddenly at a temperature of 175°, the crystals being then truly cubic ; on cooling, the birefringence reappears. Sp.gr. 2·34, hardness 6–7, refractive index 1·49, birefringence 0·0005.

Quartz when heated passes into β-tridymite at 870°, and this in turn passes into β-cristobalite (or metacristobalite, the cubic, optically isotropic modification) at 1470°. On cooling, the latter passes into the birefringent α-cristobalite at 180°–270°. The refractive index of this artificial cristobalite is about 1·484, being slightly higher than that of tridymite (1·477) ; m.p. 1710°. Cubic crystals of silica have also been obtained artificially by heating an aqueous solution of colloidal silica with hydrofluoboric acid at 200° under a pressure of 26 atmospheres. Cristobalite has also been detected in silica bricks. L. J. S.

CRITH. The weight of a litre of hydrogen at 0° and 760 mm. pressure—viz. 0·0896 gram.

CROCEIN, BRILLIANT, ORANGE, SCARLETS, v. AZO- COLOURING MATTERS.

CROCEINE ACID, 2-Naphthol-8-sulphonic acid. Used in making croceine scarlet and other dyes.

CROCIDOLITE. (*Krokydolith,* Ger.) A mineral of the soda-amphibole group, consisting of sodium and iron (ferric and ferrous) silicate, $NaFe'''(SiO_3)_2\cdot Fe''SiO_3$. It is known only in a finely fibrous form, its name, in fact, being from κροκύς, κροκύδος, wool. In the trade it is known as *blue asbestos,* and it is worked for the same purposes as the other varieties of asbestos (q v.). It is, however, more readily fusible (to a black magnetic glass) than are tremolite-asbestos and serpentine-asbestos. The mineral has been long known from the Asbestos Mountains near the Orange River in Griqualand West, South Africa, where it occurs abundantly as veins, 1 or 2 inches in thickness, in jasper-schists. The closely aggregated parallel fibres are arranged perpendicularly or nearly so to the walls of the veins ; and the material is extracted as slabs. It is now extensively mined for commercial purposes (H. F. Olds, Trans. Inst. Mining and Metall. 1899, vii. 122 ; G. E. B. Frood, The Cape Asbestos Industry, Ann. Rep. Govt. Mining Engineer, Dept. of Mines, S. Africa, 1915, and S. African Mining Journal, 1916).

Being an alkali silicate with ferrous iron, crocidolite is especially liable to decomposition when exposed to weathering ; sodium is removed, and the iron oxidised and hydrated to form limonite, while the silica is set free. There then results a ferruginous quartz possessing the finely fibrous structure of the original mineral ; or, in other words, a pseudomorph of quartz and limonite after crocidolite. This material is coloured a rich golden yellow, and displays a silky lustre, and being at the same time very hard, it is well adapted for ornamental purposes. When cut and polished with a convex surface, it displays a cat's-eye effect, and it is extensively used for making knobs, umbrella handles, beads, &c. Such material is known as *tiger-eye,* though, unfortunately, in the trade the name crocidolite is very frequently misapplied to it. The name *pseudo-crocidolite* would be more appropriate. In some stones there has been silicification without oxidation, and the indigo-blue colour of the original crocidolite has been preserved : material of this kind is known as *hawk's-eye.* The stones have sometimes been coloured artificially by the same processes as adopted in the staining of agate (q.v.).

L. J. S.

CROCOITE or **Crocoisite.** Lead chromate, $PbCrO_4$, crystallising in the monoclinic system. The name was originally given in the French form crocoise by F. S. Beudant in 1832, from κρόκος, saffron ; this was later changed to crocoisite, and afterwards to the more correct form crocoite. This mineral is the only chromate of any importance found in nature, and in it the element chromium was discovered. It is found usually as crystals which are bright hyacinth-red in colour with a brilliant lustre ; the streak is orange-yellow. On exposure to light the crystals soon deteriorate in translucency and

brilliancy. Sp.gr. 6·0, H. 2½–3. Crocoite is a mineral of secondary origin in veins of lead ore and is often associated with gold. It is found at Beresovsk in the Urals (where it was discovered in 1766), Congonhas do Campo near Ouro Preto in Brazil, Luzon in the Philippines, Umtali in Rhodesia, and as very fine crystals at Dundas in Tasmania. The mineral has been used as a pigment, being identical in composition with the artificial product chrome-yellow.

L. J. S.

CRONSTEDTITE v. THURINGITE.

CROOKESITE. A selenide of copper, thallium (Tl 16–18 p.c.), and silver forming compact masses with lead-grey colour and metallic lustre. Sp.gr. 6·9, H. 2½–3. It occurs embedded in calcite in the Skrikerum mine, Smäland, Sweden. Although a rare mineral it is of interest in being one of the few minerals containing thallium in considerable quantity. L. J. S.

CROPS. The composition of crops may be regarded from two points of view : (1) the materials they contain, which render them valuable either as food or as sources of some substance of commercial value ; (2) the materials they remove from the soil, which must eventually be replaced if the fertility of the land is to be maintained.

In Table I, the composition of some of the principal crops grown in the United Kingdom is set out, cereals being excluded because they are dealt with separately. The composition of each of these materials shows considerable variations, and the analyses given are either typical or the means of a small number of determinations.

TABLE I.—PROXIMATE COMPOSITION OF CROPS.

	Water	Crude fat	Protein crude	Carbo-hydrates	Crude fibre	Ash
Leguminous :						
Field beans	13·49	1·68	25 31	48·33	8·06	3·13
„ „ haulm	18·40	1 10	8·10	31 00	36·00	5·40
Field peas	13 92	1·89	23·13	52 68	5·68	2·68
„ „ haulm	13 60	1·60	9 00	33·70	35 50	6·60
Clover hay	16 50	2·90	13 50	37 10	24·00	6·00
Lucerne hay	16 50	2 60	14 20	29·20	29·50	8·00
Vetches, green	82·50	0 50	3 20	7 20	5·10	1·50
Root crops :						
Potatoes	74·98	0·15	2 08	21·01	0 69	1·09
Mangolds	87 50	0 14	1 34	8·90	0 98	1·14
Sugar beet	75 00	0·10	1·30	21 40	1 50	0 70
Swede turnips	87·80	0 21	1 54	8·22	1·32	0·91
White turnips	90·78	0·22	1 18	5·89	1·13	0·80
Fosterton hybrid turnips [1]	91 30	—	0 79	6·47	0·94	0·50
Aberdeen yellow [2]	91·09	—	1·14	6 08	1·03	0·66
Carrots	86·79	0 30	1 23	9 17	1·49	1·02
Meadow hay	14 30	2·50	9 70	41 40	26 30	6·20
Seeds, hay	14·30	2·70	10 20	36 10	30 20	6 50
Mustard, green	85 10	0 40	2·90	7 30	2·90	1·40

Leguminous crops. The leguminous seeds are distinguished by their high protein content The proteins of the bean and pea and similar seeds have been studied by Ritthausen (Eiweisskörper der Getreidearten, Bonn, 1872) and Osborne (J. Amer. Chem. Soc. 1898, 20, 410 ; Amer. J. Physiol. (1908, 23, 180, &c.). The most abundant of these is the so-called legumin (q v.), which, according to Osborne, is a globulin containing lysine. Lentils contain a conglutin which has been hydrolysed, also some edestin.

The leguminous seeds grown in this country contain but a small proportion of oil, which has rot received any special examination ; the soya bean, however, yields oil up to 20 p c., and is extensively imported from Manchuria and pressed for oil (v. SOYA BEAN).

The only carbohydrate in beans, peas, &c., that has received any attention, is the starch, which is abundant and the granules of which possess characteristic shapes. The ash of leguminous plants is distinguished by a large proportion of lime, as may be seen from analyses 5–10 in Table II.

[1] Aitken, Trans. H. & Ag. Soc. 1884, 16.
[2] Wilson, *ibid.* 1886, 18.

Root crops. In these materials, the ether extract contains little, if any, true fat, the nitrogen-containing substances are also very far from being all protein ; usually one-half or more of the nitrogen present is combined in various non-protein forms.

Potatoes.—The characteristic carbohydrate is starch, of which there may be over 20 p.c. ; but sugars (both sucrose and reducing sugars) may be present up to 1 p c., and dextrins or amylans are also present in about the same amount. Amongst the nitrogen compounds there are both insoluble and soluble proteins, part of the latter being coagulable by heat or acids, and a large range of amino- bodies, among which tyrosin has been identified. The non-protein nitrogen may amount to more than half the total nitrogen. The darkening of the juice of a fresh potato is due to the black substance formed by the oxidation of the tyrosine under the action of an enzyme, also present in the cells. The darkening of boiled potatoes is due to some other cause (Ashby, J. Agric. Sci. 1905, i. 348). About two-thirds of the ash of potatoes consist of phosphoric acid and potash.

Mangolds.—The characteristic carbohydrate

present in the mangold is sucrose, which constitutes about 8 p.c. of the weight of the root, the total dry matter amounting to about 13 p.c. About 0·25 p.c. of reducing sugar is also present. The variation in the sugar content of mangolds has been examined by Wood (J. Agric. Sci. 1905, 1, 176), who gives the following table :—

Variety	Yield per acre—tons	Dry matter p.c	Sugar p.c.	Nitrogen p.c.
White-fleshed globe .	29 9	10·7	6·3	0·165
„ „ intermediate	27 4	12·0	7·1	0·168
Yellow-fleshed tankard .	24 6	13·1	8·0	0 186
„ „ globe. .	25 0	13·4	8·2	0 191
Long red . .	29 9	13·1	7·9	0·157

Of the nitrogen in mangolds, only 30–50 p.c. is in the protein form, 20–40 p.c. is combined as amide or amino- acid and is liberated on hydrolysis as ammonia, while 10 p.c. may be in the nitric form.

On storage, the mangold loses sugar by respiration, and some of the sucrose becomes changed into reducing sugar, a process which is much accelerated as soon as the temperature rises in the spring (*see* Miller, J. Roy Agric. Soc. 1900, 61 ; 1902, 63).

Sugar beet.—In the sugar beet, which has been derived from the same species of *Beta* as

the mangold, the characteristic carbohydrate is likewise sucrose, which may be present to the extent of 20 p.c. It is always accompanied by a certain proportion of reducing sugars (glucose and maltose), which, in well-grown roots, should not exceed 1 p.c. of the sucrose.

The variations in the amount and nature of the sugars in sugar beet have been subjected to very detailed investigation, for accounts of which the numerous technical works dealing with the beet-sugar industry, should be consulted. *V.* SUGAR.

The nitrogenous constituents resemble those of the mangold (*see* Lippmann, Ber. 1896, 29, 2645).

Swedes and turnips.— In these closely allied roots, the carbohydrates consist of sugars (chiefly reducing sugars, though few data exist) and pectic bodies yielding a mucilage on boiling with water. In Wilson's analyses, already quoted, the sugars averaged 4·72 p.c. The nitrogen compounds are also largely non-protein, only from 30 to 50 p.c. consists of protein. It is generally considered that swedes and turnips grown in the north and especially in the east of Scotland, possess a higher feeding value than the roots grown in the south ; analytical data to confirm this opinion are, however, lacking, though it is certain that much larger crops are usually grown in the cooler climate of the north, where the crop can be sown earlier with success.

Ash of crops. In Table II. are collected various analyses of the ash of the crops above mentioned.

TABLE II —COMPOSITION OF THE ASH OF FARM CROPS.

	Ash in dry matter	N in dry matter	Fe₂O₃	CaO	MgO	K₂O	Na₂O	P₂O₅	SO₃	Cl	CO₂	SiO₂
1. Potatoes .	3·99	0·88	0·35	1·53	3·48	58·27	0 06	12·86	5·87	7·27	11·37	0·58
2. Mangolds .	6·70	1·31	0·44	3·58	2·13	35·90	19·34	9·34	3·25	3·87	21·43	0·97
3. Swedes	5·58	2·31	0·61	12·12	3·02	39·17	5·24	9·83	13 49	2·48	12·43	0·72
4. Grass .	7·21	1·65	0·49	12·48	3·83	29·76	4·09	7·04	6·17	8·78	10·31	18·32
5. Clover .	8·15	2·92	1·03	37·37	5·10	13·10	0·58	3·75	1·82	2·26	34·96	0·54
6. Beans, corn	3·27	4 32	0·48	5·60	6·61	40 58	2·12	30·69	6·35	2·43	5·28	0·41
7. „ straw	5·80	0·94	1·54	28·39	3·12	8·07	14·57	2·31	3·30	2 49	33·68	3·08
8. Peas, corn	2·53	3·87	0·07	5·74	8·97	44·31	0·39	29·30	10·42	0·45	—	0·37
9. „ straw	5·87	—	1·03	40·34	8·30	11·78	9·90	8·26	6·76	3·84	—	10·66
10. Lucerne .	8·71	—	2·68	24·74	6·27	41·91	1·22	7·71	5·63	8·05	—	3·16
11. Flax, seed	3·82	—	1 54	10·96	11·47	27·85	4·15	41·27	2·01	0·63	—	1·47
12. „ stem	3·70	—	6·62	25·16	4·99	25·56	10·16	8·94	4·02	6·64	—	9·40
13. Hops, cones	11·25	—	1·80	16·77	5·66	28·35	1·99	13·73	5·01	4·35	—	22·32
14. „ leaves	18·00	—	0·64	40·17	5·32	13·65	3·79	7·82	3·49	4·02	—	22·21
15. „ stems	4·70	—	1·07	29·59	8·34	26·18	5·06	11·23	3·41	8·87	—	8·29
16. Tobacco .	16·27	—	2·93	42·34	11·22	17·48	4 26	3·22	4·28	4·87	—	10·11

Analyses 8–16 are means taken from Wolff's Aschen-analysen, and have been recalculated to exclude the carbon dioxide present in the ash, as obtained after burning. Analyses 1–7 are selected from the Rothamsted records.

Materials removed from the land by average crops. Table III., compiled by Warington from Rothamsted data, shows the amount of the three important constituents—nitrogen, phosphoric acid, and potash, which would be contained in an average crop of the magnitude indicated, and therefore have been removed

from the soil by the crop, except in the case of the nitrogen contained in leguminous crops.

A comparison of these figures with the amount of fertilising material usually provided for the crops in question, or the effects of particular manures in field experiments, serves to show that the data contained in Table III. afford no guidance in deciding the appropriate manure for each crop.

The earliest theory of plant manuring, that of Liebig, supposed that the requirements of the plant can best be satisfied by applying to

TABLE III.—AMOUNT OF FERTILISING CONSTITUENTS PER ACRE REMOVED BY AN AVERAGE CROP.

—	Weight of crop, dry	Nitrogen	Potash	Phosphoric acid
	lbs.	lbs.	lbs.	lbs.
Wheat, 30 bushels, straw 28 cwts.	4183	50	28·8	21·1
Barley, 40 ,, ,, 22 ,,	3827	49	35·7	20·7
Oats, 45 ,, ,, 25 ,,	3978	52	46·1	19·4
Maize, 30 ,, ,, 19 ,,	3377	43	36·3	18·0
Meadow hay, 1½ tons	2822	49	50·9	12 3
Red clover hay, 2 tons	3763	98 [1]	83·4	24·9
Beans, 30 bushels, straw 20 cwts.	3461	107 [1]	67·1	29·1
Turnips, 17 tons, leaf 5 tons	4657	110	148·8	33·1
Swedes, 14 ,, ,, 2 ,	4055	98	79·7	21·7
Mangolds, 22 ,, ,, 8 ,,	7568	149	300·7	52·9
Potatoes, 6 ,, tubers	3360	46	76·5	21·5

the land exactly the constituents taken away by a good crop of that particular kind ; but the results of the Rothamsted experiments, confirmed by general farming experience, very soon showed that this view was incorrect, because it failed to take into account the enormous amount of plant food contained in the soil, more or less of which would reach the plant according to the method of cultivation and the plant's habit of growth. Moreover, in practical farming the supply of manure is largely determined by the place the crop occupies in the rotation and the treatment which has been given to the previous crops. To take an example, wheat and barley withdraw almost the same fertilising materials from the soil, yet all farming experience goes to show that the yield of wheat is chiefly determined by the supply of nitrogen If this element is present in sufficient quantity the wheat plant with its long period of growth is usually able to satisfy its requirements for phosphoric acid and potash from the soil. With barley, nitrogen is still a most important element in nutrition, but phosphoric acid also exerts a striking beneficial action and is a necessary element in the fertiliser. Neither for wheat nor barley need potash be supplied except on very light soils. A still more noteworthy example is provided by the swede turnip crop. The table shows that an average crop will take away from the soil about 100 lbs. of nitrogen, 20 lbs. of phosphoric acid and 80 lbs. of potash, yet the usual fertilisers applied to swedes consist almost wholly of phosphatic compounds, with a comparatively small amount of nitrogen and no potash. The majority of the swedes grown in this country receive from 50 to 100 lbs. of phosphoric acid (i.e. about 5 cwt. of superphosphate or basic slag), and the small quantity of nitrogen that would be provided by a light dressing of farmyard manure or half a hundredweight of sulphate of ammonia. The fertiliser requirements of a crop are in fact conditioned by its specific habit and by the soil (q.v.) rather than by its composition. Certain broad characters may be distinguished. Cereal crops possess considerable powers of obtaining the phosphoric acid and potash reserves in the soil provided they are well supplied with active forms of nitrogen. Leguminous crops rarely require a nitrogenous fertiliser, but respond to mineral fertilisers and particularly to potash, the soil also should be neutral and well supplied with lime. Cruciferous crops are particularly de-

pendent upon an abundant supply of phosphoric acid. Crops elaborating a considerable amount of carbohydrate, e.g. mangolds and potatoes, require potash. In general it may be said that nitrogen promotes leafy development, phosphoric acid maturity, and potash carbohydrate formation and continued growth.　　A. D. H.

CROTON OIL is obtained from the seeds of *Croton Tiglium* (Linn.), a tree belonging to the *Euphorbiaceæ*, indigenous to the Malabar coast, and cultivated in Southern Asia and China. The seeds contain 53–56 p c. of oil.

The oil has an amber-yellow, orange, or brown colour, according to its age ; it has a nauseous odour, a burning taste, and acts as a very powerful purgative. It blisters the skin and mucous membrane.

The chemical composition of croton oil differs so widely from that of all other oils, that its recognition, by means of the ' quantitative reactions ' (see OILS AND FATS), is easy. It contains a considerable amount of volatile acids ; its Reichert-Meissl value is about 13 ; its iodine value is 102–106. Saponification value, 210–215 ; and specific gravity, 0·940 to 0 960. Croton oil is strongly dextro-rotatory ($+14·5°$ to $16·4°$).

The variations in the recorded values are mainly attributable to different methods of extraction Croton oil contains the glycerides of tiglic acid, acid of butyric, caproic, lauric, myristic and palmitic acids, and probably also oleic acid. The vesicating principle is a resinous substance, $C_{13}H_{18}O_4$ (Dunstan and Boole, Proc. Roy. Soc. 1895, 58, 238).

CROWBERRY (*Empetrum nigrum*). The leaves of the crowberry contain a wax composed of ceryl cerotate, benzoic acid, urson, tannin, dextrose and probably rutin. The anhydrous urson $C_{16}H_{16}O$ is identical with that obtained from the leaves of *Uva Ursi*. *Empetrum nigrum* contains no alkaloids, andromedextrins or glucosides decomposed by emulsion (Van Itallie, Pharm. Weekblad, 1918, 55, 709).

CROWN GLASS v. GLASS.

CRUCIBLES. A perfect crucible should withstand the highest temperatures without fusion, should bear sudden changes of temperature without fracture, and should be unacted upon by the materials which are to be heated in it. A semi-automatic apparatus for moulding crucibles has been patented by Sims (Eng. Pat. 445, 1888).

[1] Wholly or in part derived from the atmosphere.

Clay crucibles are prepared from selected clay ; of the Stourbridge clay worked, only about 5 p.c. is available for this purpose. Its plasticity is much increased by exposure for some months in a moist condition to the air. During this process of ' weathering ' it becomes disintegrated, and the removal of foreign matter is thereby facilitated. The presence of iron pyrites is especially injurious ; furnace gases convert it into the oxide which acts as a flux and forms cavities in the crucible. Lime is also hurtful, except when in very small quantities and uniformly distributed. Potash and soda are invariably present in clay, and when in small quantity increase the coherence of the crucible without appreciably impairing its power of withstanding the action of heat.

In order to reduce the tendency to crack, and to increase its refractory character, the clay is usually mixed with sand, ground flints, burnt clay (old broken crucibles), graphite or coke These, which are either less fusible than the clay or altogether infusible, form a skeleton which upholds and prevents deformation of the crucibles at temperatures at which the clay would tend to fuse. The most refractory crucibles contain the largest proportion of silica

The clay, which should be of the greatest possible fineness, is well beaten to remove air bubbles and mixed with the proper quantity of the refractory material According to Berthier (Traité des Essais, 1, 66), when silica is used, it should not be too fine, as the tendency to combine with the clay and thus increase the fusibility would thereby be increased. Crucibles of fine grain are also more liable to fracture

Small crucibles are usually baked in a kiln, but the large casting pots of Stourbridge clay are not baked until immediately before use. When the temperature of the baking is high, the crucible is more liable to fracture on reheating.

All clay crucibles are more or less acted upon by litharge, but metals and most ores may be heated in them without danger. Berthier recommends a lining of such material as silica, alumina, or magnesia previously moistened. A lining of chalk renders a crucible less permeable to litharge.

Queneau recommends lining clay crucibles, before drying, with some substance which will resist the chemical reactions for which they are designed and then compressing strongly, drying, and firing (Fr. Pat. 354319 ; J. Soc. Chem. Ind. 1905, 1071).

Crucibles may be rendered non-porous by treating with ferrous sulphate solution and firing (Mitchell, U.S. Pat. 894845 ; J. Soc. Chem. Ind. 1908, 886) or by the addition to the clay of chromic oxide, chromates or chrome iron ore, which also renders them much more refractory (Bach, Eng. Pat. 24041, 1903 ; Klein, U.S. Pat. 787770 ; Seigle, Fr. Pat. 383593 ; and Placet, Eng. Pat. 28728, 1896).

The fracture of crucibles by expansion of solidifying metal can be prevented by lining with friable ferrous material (Colby, U.S. Pat. 830208 ; J. Soc. Chem. Ind 1906, 934).

Goldschmidt recommends that crucibles for the ' Thermit ' process should be lined with a mixture of magnesia or carborundum and soluble glass (Fr. Pat. 354597 ; J. Soc. Chem. Ind. 1905, 1114).

Very large crucibles may be built up from cylinders or annular rings of refractory material, provided arrangements are made for tapping the contents without moving the crucible (Reynolds, Eng. Pat 1004, 1901 ; Rousseau, Eng. Pat. 7451, 1902).

Stourbridge clay crucibles are made from a mixture of raw ground clay with about one-half its weight of powdered, sifted, old glass pots, from which all adherent glass has been removed, the mixture being made in a disc mill, and kneaded to the proper consistency. Percy gives the composition of the Stourbridge clay used for the best crucibles as silica, 79·25 ; alumina, 13 57, iron oxide, 1·38 ; lime, 0·08 ; magnesia, 0·42 ; water, 5 11.

The following analyses show the composition of certain varieties of crucibles. Nos. 1–7 are by Berthier, No 8 by Dick, Nos. 9–12 by Brand, and Nos 13–15 by Méne – -

	Silica	Alumina	Iron oxide	Magnesia	Lime	Potash	Sulphur	Carbon	Water
1. French, made by Beaufay at Paris	64·6	34·4	1·0	—	—	—	—	—	—
2. French, made by Deyeux at Savignes	72·3	19 5	3·9	—	—	—	—	—	1·8
3. Hessian	70·9	24·8	3·8	trace	—	—	—	—	—
4. English steel	71·0	23·0	4 0	—	—	—	—	—	—
5. St. Etienne steel	65·2	25·0	7·2	trace	—	—	—	—	—
6. Glass pots, Nemours	67·4	32·0	0·8	trace	—	—	—	—	—
7. ,, ,, Bohemia	68·0	29·0	2·2	0·50	—	—	—	—	—
8. Cornish, made by Juleff	72·39	25·32	1·07	trace	0·38	1·14	—	—	—
9. Steel crucible ; clay	53·92	40·57	—	—	—	—	0·230	—	—
10. ,, ,, coke clay	42·78	34·71	—	—	—	—	0·490	18·60	—
11. ,, ,, graphite	24·63	27 89	—	—	—	—	0·270	40 43	—
12. Magnesia	4 80	2·49	—	92·62	—	—	0·099	—	—
13. English blacklead	51·4	22·0	3·5	—	0·2	—	—	20·0	1·8
14. Ditto	45·1	16·65	0·95	—	—	—	—	34·5	2·5
15. Ditto	50·0	20·0	1·5	—	0·5	—	—	25·5	3·0

Hessian crucibles are composed of equal weights of Almerode clay and sand. They are usually triangular, of coarse texture, porous, rapidly destroyed by litharge, and liable to

fracture on sudden change of temperature, but will withstand a very high degree of heat.

French crucibles are made from a mixture of 1 part raw Ardennes clay and 2 parts of the same which has been burnt. They are refractory and of fine texture.

Cornish crucibles are largely used for copper assaying. They are round, of coarse grain, and of a mottled greyish-white colour. They are kiln-burnt, and withstand sudden changes of temperature, but cannot be heated to whiteness. Cornish crucibles are now made by the Morgan Crucible Company at Battersea.

London crucibles are of reddish-brown colour and close texture. They will not stand sudden change of temperature, but withstand the action of litharge fairly well.

Silica crucibles may be made of powdered silica, mixed with a highly absorbent substance, e.g. kieselguhr, saturated with water (Sankey, Eng. Pat. 3353, 1906; J. Soc. Chem. Ind. 1907, 96). Sand, mixed with a small proportion of cement and water, moulded, dried, and heated to the fusing-point of the sand, forms a very refractory material (Reppey, U.S Pat 905295; J. Soc. Chem. Ind. 1909, 24) A mixture of sand with a little lime may be used (Berglund, Fr. Pat. 366830; J. Soc Chem. Ind 1906, 1081).

White fluxing pots are made by the Morgan Company from a highly refractory fire-clay from Rouen. Crucibles containing carbon are now largely used. For very high temperatures, crucibles cut from a block of gas carbon or similar material may be employed. Clay crucibles may also be filled with a moist mixture of charcoal with starch, treacle, gum-water, or oil, or, for large crucibles, gas tar. The mass is forced with considerable pressure into the crucible and is then cut out, leaving a coating of about ½ inch in thickness, or the coating is put into the crucible and smoothed with a glass rod. The crucible is then filled with powdered charcoal and heated to redness.

Graphite crucibles. For the fusion of metals, plumbago or coke crucibles are of great value, but they are not largely used for assaying At the Battersea works, the following process of manufacture is employed : hand-picked Ceylon plumbago is ground, sifted, digested with dilute sulphuric acid to remove the greater part of the iron, and mixed and kneaded to a stiff paste, with about an equal weight of fine fireclay. The mixture is passed through a pug-mill, and is cut into blocks. When required for use, the blocks are again passed through the mill, and made by hand on a wheel or moulded by machinery. They are then dried and baked in saggars. These crucibles may be protected from oxidation by lining them with clay (Woolford, Eng. Pat. 24479, 1898; J. Soc. Chem. Ind. 1900, 52; McDonald, U.S. Pat. 828954; J. Soc. Chem. Ind. 1906, 911).

They are of fine grain, and will withstand the highest temperatures and repeated sudden changes. The graphite is slowly oxidised by metallic oxides or by the furnace gases. To minimise this, the crucible may be coated by dipping in a paste of clay and solution of borax. Any iron which is present in the graphite is liable to become introduced into the melt, and the carbon itself combines with iron or steel (v. Brand, Chem. Zentr. 15, 407; and Dingl. poly. J. 256, 227).

Tar, rosin, &c., may be used to bind the clay and graphite in manufacturing these crucibles (Putz, D. R. P. 181979; J. Soc. Chem. Ind. 1907, 1030). Digby recommends (Eng. Pat. 3661, 1893) the following composition :—

Plumbago, 17-mesh granules . 17 parts
Plumbago, 80- ,, ,, . 2 ,,
Russian clay . . . 5 ,,
China-stone. . . . 5 ,,
Gas carbon . . . . 2 .,

The last three ingredients are ground and mixed with water and then the plumbago is added and the crucibles formed, dried at 65° and baked.

Salamander crucibles, made by the Morgan Company, contain a much smaller proportion of carbon. They withstand sudden changes of temperature perfectly.

Lime crucibles are cut from blocks of well-burnt (preferably slightly hydraulic) lime.

Magnesia was introduced by Caron as a refractory basic material for making crucibles or for lining reverberatory furnaces for melting and dephosphorising steel Magnesia contracts considerably when heated ; it is therefore necessary, before making it into bricks or crucibles, to expose it to a higher temperature than that to which it will be heated. The strongly calcined magnesia is made into a paste with 15-30 p.c. of raw (slightly calcined) magnesia, and 10-15 p.c. of water, and is moulded, dried, and baked at a red heat. The highly heated magnesia would not cohere without admixture with the raw material. Magnesia crucibles are not injured by exposure to the atmosphere. Gaudin makes crucibles from a mixture of 1 part magnesia and 1 part bauxite. They may also be formed from a mixture of calcined magnesite with from 2 p.c. to 12 p.c. of a boron compound (according to the amount of calcium present), moistened, moulded, dried and fired at a high temperature (Rawson and Littlefield, Eng Pat. 16004, 1900 ; J. Soc. Chem. Ind. 1901, 992, and ibid. 1902, 52) The crucible is said to resist molten litharge. Porous crucibles for metal refining, are made from a similar mixture with the addition of sawdust (Dobell, Eng. Pat. 10715, 1897).

Alumina crucibles withstand sudden changes of temperature, and are not affected by the materials fused, even sodium being without action. According to Deville's process (Ann. Chim. Phys. [3] 46, 195), alumina precipitated at low temperature from ammonia alum solution is mixed with an equal weight of powdered marble, and is exposed to the highest temperature of a wind furnace. The mixture so produced, which may be considered as consisting of calcium aluminate, is mixed with its own weight of moist, precipitated alumina, and is made into a crucible, dried and baked (see also Caspar, U.S. Pat. 886111 ; J. Soc. Chem. Ind. 1908, 568). When the crucible is required to withstand higher temperatures, the amount of the calcium aluminate may be reduced, but the proportion of lime should not fall below 10 to 20 p.c.

Bauxite has been used to replace alumina. It is extremely refractory (v. Bauxite, art. ALUMINIUM).

Carborundum crucibles are infusible and

resistant to chemical action and have great solidity. They may be made from a mixture of commercial carborundum with sufficient clay to render it plastic (Velter, Fr. Pat. 376179 ; J. Soc. Chem. Ind. 1907, 1010 ; Engels, Eng. Pat. 14567, 1901).

A mixture of powdered silica rock or ganister with carborundum or amorphous silicon carbide, may be used. It is mixed with water-glass solution or glue, &c., compressed to shape and heated to the temperature of the electric furnace (Imray and Carborundum Co. Eng. Pat. 19493, 1902 ; 3308, 1903) (*see also* CARBORUNDUM).

(*See* further, Kerl, Handb. Thonvaaren Ind. 1879, 528–534 ; and Percy, Metallurgy (Fuel, &c.), 1875, 110–141).

CRUMPSALL YELLOW *v.* AZO- COLOURING MATTERS.

CRURIN. Trade name for quinoline bismuth thiocyanate, used as an antigonorrhoic.

CRYOGENIN. *m* - Benzaminsemicarbazide

$$H_2N—CO--\langle\bigcirc\rangle—NH·NH·CO·NH_2.$$ Used as
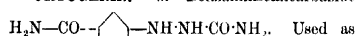
an antipyretic.

CRYOLITE.—(*Kryolith*, Ger.) A native fluoride of aluminium and sodium, found almost exclusively in Greenland, whence it has been sometimes called ' Greenland spar.' The name cryolite, or ' ice-spar ' (*Eisstein*) refers to the general resemblance of the mineral to ice ($\kappa\rho\nu\sigma$) and to its ready fusibility in a candle-flame. The mineral was discovered by the Danes in 1794, and described in the following year by Schumacher. Nearly all the cryolite of commerce is obtained from a single locality at Ivigtut (or Evigtok), on Arsuk-fjord in south-west Greenland. This locality was visited by Giesecké, and later by J. W. Tayler (Quart. Jour. Geol. Soc. 12, 140). The cryolite occurs as a large deposit in gneiss, and contains (especially near its junction with the enclosing rock) a number of metallic minerals, such as galena, pyrites, and chalybite (*v.* P. Johnstrup, N. Jahrb. f. Min. 1886, 1, Ref. 28 ; R. Baldauf, Zeitsch. prakt Geol. 1910, xviii. 432 ; O. B. Bøggild, Mineralogia Groelandica, Kjøbenhavn, 1905 ; O. B. Bøggild, Meddelelser om Grønland, 1912, 1 107, and Zeitsch. Kryst. Min., 1913, h. 591. C. P. Bernard, The Cryolite Mine at Ivigtut, Greenland, Mining Magazine, 1916, xiv. 202).

Cryolite is usually found in cleavable translucent masses, of snow-white colour, with a peculiar moist-looking vitreous lustre which renders the mineral easy of recognition. H. 2·5 ; sp.gr. 2·9–3. Crystals are rare, and their relations have been the subject of much discussion ; they are cube-like in habit, and belong to the monoclinic system. There are three perfect cleavages approximately at right angles to one another. Although cryolite is usually white, it is sometimes coloured brown or reddish, and is said to pass downwards, in the Greenland deposit, into a black mass. The black variety loses its colour when heated. Before the blowpipe cryolite fuses to a white enamel.

The composition of cryolite may be represented by the formula 3NaF·AlF₃ or Na₃AlF₆. This corresponds to 12·8 p.c. Al, 32·8 Na, and 54·4 F. An analysis of the Greenland cryolite by Chodnev yielded 13·23 p.c. Al, and 32·71 Na, with 0·83 of Mn₂O₃ and MgO (Verh. Petersb. Min. Ges. 1845–6, 209). Durnev found in the cryolite of Miask in the Urals, 13·41 p.c. Al, 32·31 Na, 0·55 Fe₂O₃ and Mn₂O₃, and 0·35 CaO (Pogg. Ann. 83, 587). Deville found in the Greenland cryolite 0·018 p.c, of vanadic acid and a small proportion of phosphoric acid. An analysis of cryolite from near Pike's Peak, Colorado, by Cross and Hillebrand yielded Al 12·9, Na 32·4, F 53·55, Fe₂O₃ 0·4, Ca 0·28, H₂O 0·3 (Amer. J. Sci. 1883, xxvi. 271).

Cryolite was formerly a rare mineral, but about 1855 it was introduced into Europe commercially, and at once found numerous applications in the arts. About 10,000 tons are exported annually from Greenland. By heating finely powdered cryolite with sodium or with magnesium, J. Percy and A. Dick obtained metallic aluminium (Phil. Mag. 10, 1855, 364). Deville found that fused cryolite is decomposed by the passage of an electric current, with elimination of free aluminium. At the present time, aluminium is prepared by the electrolysis of bauxite, but the addition of some cryolite is necessary to start the process and to keep it in continuous operation (*v. Aluminium*).

A wide range of applications was suggested when Julius Thomsen showed in 1850 that cryolite is readily decomposed by heating with calcium carbonate, and that sodium aluminate may be thus obtained :

$$Al_2F_6·6NaF+6CaCO_3$$
$$=3Na_2O·Al_2O_3+6NaF_2+6CO_3$$
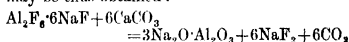
If heated with quicklime, a similar decomposition is effected, of course without evolution of CO₂. The sodium aluminate has been used in the manufacture of alum, and in the preparation of caustic soda for soap making. By lixiviation, the aluminate is easily dissolved out ; and by the passage of CO₂ through the solution, Na₂CO₃ is obtained, while alumina separates in a gelatinous form. The decomposition of cryolite may also be effected by boiling the finely pulverised mineral with milk of lime. By adding an excess of powdered cryolite to the resulting solution, the aluminate is decomposed, the alumina being precipitated, while sodium fluoride remains in solution :

$$3Na_2O·Al_2O_3+Al_2F_6·6NaF=2Al_2O_3+12NaF$$
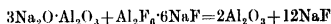
Cryolite can be readily decomposed by the action of sulphuric acid, with formation of sodium sulphate, which can be easily converted into carbonate ; but the process, after trial at Copenhagen, has been abandoned in consequence of the inconvenience arising from the evolution of hydrofluoric acid :

$$Al_2F_6·6NaF+6H_2SO_4$$
$$=Al_2(SO_4)_3+3Na_2SO_4+12HF$$
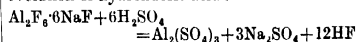
The manufacture of soda from cryolite is carried on at Oersund in Denmark, and at Natrona, near Pittsburg in Pennsylvania. The mineral is also employed in the preparation of enamels on iron and for the manufacture of an opaline glass, somewhat resembling porcelain. This glass may be formed by fusing together 100 parts of silica, 35 or 36 of cryolite, and 13 or 14 of oxide of zinc. C. Weinreb has investigated the cause of the milkiness of cryolite glass, and believes that it is due to the presence

of aluminium fluoride, which on the cooling of the fused mass, separates in a highly comminuted condition, and being distributed through the glass renders it more or less opaque (Dingl. poly. J. 256, 361).   L. J. S.

CRYOLITHIONITE. Fluoride of lithium, sodium, and aluminium, $Li_3Na_3Al_2F_{12}$, remarkable in containing a higher percentage of lithium (5·35 p.c.) than any other mineral. It occurs as large, colourless, rhombic-dodecahedra embedded in the cryolite deposit at Ivigtut in Greenland. Sp.gr. 2·77 ; H. 2½–3 ; n_{Na} 1·3395 ; m.p. 710°. The mineral dissolves in 1350 parts of water at 18°, and from this solution crystallises as cubes.   L. J. S.

CRYOSCOPY. So long ago as 1788 Blagden proved that the extent to which the freezing point of an aqueous solution lies below that of water—the depression of the freezing point, as it is called—is proportional to the concentration of the dissolved substance. Nearly a century later, the researches of de Coppet and Raoult showed that when equimolecular proportions of different substances are dissolved in equal quantities of a given solvent, the solutions so obtained have, in general, the same freezing point. It is on these facts that the use of the cryoscopic method of determining the molecular weights of dissolved substances is based.

In comparing the effects of different substances on the freezing point of a given solvent, it is obviously convenient, in view of de Coppet's and Raoult's results, to refer these effects to 1 gram molecule of solute and to some definite quantity of solvent : in practice, 100 grams of the latter are taken as the standard amount. The depression of the freezing point for such a concentrated solution as one containing 1 gram molecule of solute in 100 grams of solvent cannot be determined directly : it is calculated from the depression observed for a dilute solution, on the basis of the proportionality between depression and concentration. An example may be taken to illustrate this point. A solution containing 0·609 gram of ethyl alcohol in 100 grams of water freezes 0·243° below the freezing point of water ; from these data it follows, if proportionality between depression and concentration is assumed, that the depression for a solution containing 1 gram molecule of alcohol in 100 grams of water would be $\frac{0·243 \times 46}{0·609} = 18·4°$. Again, a solution of 4·276 grams of sucrose in 100 grams of water, freezes 0·237° below the freezing point of water ; from these data it follows, as above, that the depression for a solution containing 1 gram molecule of sucrose in 100 grams of water would be $\frac{0·237 \times 342}{4·276} = 19·0°$. If the depressions produced by 1 gram molecule of other non-electrolytes in 100 grams of water are similarly calculated from experimental data, values are obtained which are very close to the figures already quoted. The depression, therefore, for a solution containing 1 gram molecule of non-electrolyte in 100 grams of water is a constant, independent of the particular solute : the average value of the constant for water, deduced in the empirical way just described, is 18·5°.

For each solvent, a characteristic constant

(k) can be similarly deduced from experimental data. The evaluation of this constant—the 'molecular depression of the freezing point'—is effected, as illustrated above, by the formula $k = \frac{M}{g} \cdot \Delta t$, where Δt is the depression of freezing point observed for a solution containing g grams of solute in 100 grams of solvent, and M is the molecular weight of the solute.

It has been shown by van't Hoff that, on thermodynamical grounds, the molecular depression of the freezing point for any solvent is quantitatively related to the temperature of freezing and to the latent heat of fusion. The relationship in question is $k = \frac{0·0198T^2}{\omega}$, where T is the freezing point of the solvent on the absolute scale, and ω is the latent heat of fusion per gram of the solvent. The following table shows how far the values of the molecular depression, calculated for various solvents by van't Hoff's formula, are in agreement with those deduced empirically :—

Solvent			Empirical k	Calculated k
Water	.	.	18 5°	18·6°
Formic acid	.	.	28°	27·5°
Acetic acid	.	.	39°	38·5°
Benzene	.	.	50°	52°
Naphthalene	.	.	68 5°	69°
p-Toluidine	.	.	53°	51°
Phenol	.	.	75°	74°

The formula $k = \frac{0·0198T^2}{\omega}$ is based on the assumption that, when a solution freezes, it is the pure solid solvent which crystallises out. It is not surprising, therefore, that in cases where the crystals separating from the solution contain some of the dissolved substance, e.g solutions of thiophene in benzene, the empirical value for the molecular depression, deduced in the usual way, differs considerably from the normal value. In such cases the depression observed is smaller than it would be if the pure solid solvent separated out.

When the value of k for any solvent has been ascertained, either empirically by experiments with normal substances of known molecular weight, or indirectly by van't Hoff's formula, it may be utilised in determining the molecular weights of new substances. For this purpose, the formula $k = \frac{M}{g} \Delta t$ is employed, but now k is taken as known, and M is the quantity to be evaluated ; in view of this, the equation may be written $M = \frac{k \, g}{\Delta t}$.

It is evident that a determination of the molecular weight of a dissolved substance by the cryoscopic method depends, not on the absolute freezing temperature of the solution, but on the difference between the freezing point of the solvent and that of the solution. This difference can be determined with greater accuracy than can the freezing temperatures themselves. A thermometer with a very open scale, covering only 5°–6°, is employed, and it is convenient, as suggested by Beckmann, to have a reservoir attached to the upper end of the thermometer tube, so that the quantity of mercury in the bulb and stem may be varied according to requirements. This device permits

the use of one and the same thermometer at different temperatures, and therefore with various solvents. In Beckmann's thermometer, which is the one usually employed in cryoscopic investigations, the scale degree is about 4 cm. in length and is divided in hundredths : with the aid of a lens, preferably adapted for sliding up and down the stem, it is possible to estimate 0·001°. The form of the reservoir attached to the upper end of the ordinary Beckmann thermometer is shown in the accompanying sketch. When it is desired to adjust the thermometer for experiments with any given solvent, the bulb is immersed in water of the same temperature as the freezing point of the solvent. If the top of the mercury thread should reach a steady position on the upper half of the scale, no further adjustment is needed. Should the mercury, after sufficient time has been allowed, extend beyond the scale and into the reservoir, it is necessary to detach a portion. This is effected by putting the bulb in water 2°–3° higher than the required temperature, and then gently tapping the upper end of the thermometer until the mercury hanging at the top of the reservoir is separated from the thread. On cooling down again to the freezing temperature of the solvent, the top of the thread should now come to rest somewhere on the upper half of the scale If the quantity of mercury in the bulb and stem is too small, so that when the thermometer is immersed in water of the same temperature as the freezing point of the solvent, the thread does not reach the scale or appears only on the lowest part of it, the bulb is warmed until the mercury appears at the top of the reservoir. By a throwing movement, some of the mercury at the bottom of the reservoir is jerked up to the top, where it joins the end of the thread. The bulb is then immersed in water 2°–3° above the temperature required, and the final adjustment is carried out in the way already described.

FIG. 1.

The cryoscopic apparatus commonly employed for the determination of the molecular weight of dissolved substances is that known as Beckmann's. The accuracy of this method, as ordinarily applied, is not great, the error being of the order ±5 p.c. For most laboratory purposes, however, this is sufficient, and it is only when extreme accuracy is required, as in the investigation of very dilute aqueous solutions, that special forms of apparatus have to be employed.

The essential parts of Beckmann's apparatus are seen in the subjoined diagram. A stout glass jar, holding about 1½ litres, is provided with a metal top, at the side of which is a hole for a stirrer, and in the middle of which is another hole capable of holding a large stout test-tube. 3–4 cm. in diameter. The lid and the tube are held in position by springs, as will be evident from the diagram. By means of a cork, there is fitted in the tube another, narrower one, to hold the liquid under investigation. This tube should preferably have a flat bottom, while the part of it which projects beyond the outer jacket is provided with an auxiliary side tube, and is itself widened out at the upper extremity. The cork with which this inner tube—the freezing tube, as it may be called —is fitted carries the thermometer, and allows also free passage to a stirrer. The latter is best made of stout platinum wire, but silver or nickel may be used, provided that the possibility of chemical action is excluded. The thermometer must be fitted in an accurately central position, so that the stirrer may be moved up and down without grating.
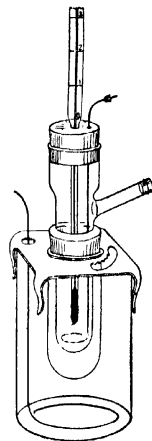
When a determination of molecular weight is to be made, the freezing tube is charged with a weighed quantity of the solvent, usually 10–20 grams, and the jar is filled with water or a mixture of ice and salt kept at a temperature

FIG. 2.

4°–5° below the freezing point of the solvent under examination. The freezing tube, with thermometer and stirrer, is immersed directly in the jar, until the temperature has fallen almost to the freezing point It is then set in the jacket tube and the contents are stirred regularly, while the mercury in the thermometer falls slowly. The fall continues until the solvent is more or less supercooled. In the majority of cases, freezing sets in spontaneously before the supercooling exceeds 0·5°, and the liberation of heat results in a rise of the mercury in the thermometer up to a steady maximum position. This is the freezing point of the solvent—the temperature at which liquid and solid solvent are in equilibrium with each other. It is advisable, when the thread is rising towards its steady position, to tap the thermometer before taking a reading, and so avoid the possibility of the mercury sticking in the capillary. Should the supercooling exceed 0·5°, crystallisation ought to be initiated, either by stirring very vigorously for a few moments or by introducing a tiny crystal of the solid solvent. Whenever freezing has begun, the solvent must then be stirred with uniform regularity until the constant temperature has been reached.

The freezing point of the solvent having been determined two or three times in the manner just described, a weighed quantity of the solute, enough to give a depression of not less than 0·2°, is introduced, and the freezing point of the solution is then ascertained in the same way as that of the solvent. Subsequent additions of solute are made and the resulting depressions determined as before. One addition, it is true, yields sufficient data for the calculation of the molecular weight of the solute, but it is desirable

to ascertain also whether the concentration of the solute has any definite and notable influence on the value obtained for its molecular weight. It is advisable, further, to redetermine the freezing point of the solvent at the end of such a series of experiments, and so obtain a guarantee that the zero of the thermometer has not changed appreciably during the course of the work.

Various suggestions have been made from time to time with the object of rendering the simple Beckmann apparatus a more accurate instrument. Thus it has been proposed to stir the contents of the freezing tube mechanically instead of by hand. The access of atmospheric moisture to a hygroscopic solvent may be prevented by passing a current of dry air into the freezing tube during an experiment, or by using as stirrer an iron ring which is enveloped in platinum foil and is operated electromagnetically. In this latter case, obviously, communication between the contents of the freezing tube and the outside air can be completely cut off. The same end is attained by employing an ordinary stirrer with a mercury valve. (For a detailed description of these modifications and additions, *see* Beckmann, Zeitsch. physikal. Chem. 1891, 7, 323; 1896, 21, 239; 1897, 22, 616; 1903, 44, 169; *also* Ostwald and Luther's Physiko-chemische Messungen.)

For the determination of the freezing point of liquids which are obtainable only in small quantities—physiological fluids, for example— Beckmann's apparatus, in its ordinary form, is too large. Modifications of this apparatus, suitable for the investigation of blood, urine, &c., have been suggested by various authors (Guye and Bogdan, J. Chim. Phys. 1903, 1, 379; Burian and Drucker, Zentr. Physiol. 1910, 23, 772). In these instruments, only 1-2 cub.cm. of liquid is required, and it is claimed that the accuracy is of the same order as that attainable with the ordinary Beckmann apparatus. In this connection, mention ought to be made also of Eykman's apparatus (Zeitsch. physikal. Chem. 1888, 2, 964; 1889, 4, 497). This consists of a small flask, holding about 10 cub. cm., into the neck of which is ground a thermometer, graduated in tenths or hundredths of a degree. There is no separate jacketing vessel, but the procedure is similar to that followed in the case of the Beckmann apparatus.

As regards the preparation of the cooling bath required in the cryoscopic investigation of aqueous solutions, the usual mixture of ice and common salt solution may be replaced in some cases by a mixture of ice and a solid salt, which gives a steady eutectic temperature. Salts suitable for this purpose, with the eutectic temperatures obtained when they are mixed with ice, are alum, $-0.47°$; sodium sulphate, $-0.7°$; potassium dichromate, $-1.0°$; potassium sulphate, $-1.5°$; copper sulphate, $-2.0°$; potassium nitrate, $-3.0°$; zinc sulphate, $-5.0°$; barium chloride, $-7.0°$. Another kind of cooling bath was used by Raoult, who surrounded the jacketed freezing tube with ether, and passed through the latter a current of dry air (Compt. rend. 1896, 123, 476; Zeitsch. physikal. Chem. 1897, 27, 617). By careful regulation of the rate at which the air is forced through the ether, the bath can be adjusted to

any point between room temperature and $-15°$.

When it is desired to find the molecular weight of a new substance, the question of the most suitable solvent arises. The choice is frequently limited by the solubility of the substance; it may be appreciably soluble in only one or two of the more common solvents. Apart from this, however, there are other considerations which must be taken into account. Extensive investigation has proved that with certain combinations of solvent and solute, the cryoscopic method gives abnormal values for the molecular weight of the dissolved substance. Pre-eminently is this the case when the solvent is water and the solute is an acid, a base, or a salt, in short, an electrolyte; under these circumstances, the value found for the molecular weight of the solute is abnormally low. On the other hand, the influence of substances containing the hydroxyl group (alcohols, acids, phenols, oximes) on the freezing point of hydrocarbons (benzene) and allied indifferent solvents, is such as to lead to abnormally high values for the molecular weight. The cryoscopic investigation of solutions of acetic acid in benzene indicates that the formula of the acid is more correctly represented by $(CH_3 \cdot COOH)_2$ than by $CH_3 \cdot COOH$. Again, while the molecular weight of alcohol in benzene is nearly normal in dilute solution, the value increases rapidly as the concentration of the alcohol rises. The combinations of solvent and solute which lead to abnormally high values of the molecular weight have been studied in detail by various workers (Auwers, Zeitsch. physikal. Chem. 1893, 12, 689; 1894, 15, 33; 1895, 18, 595; 1896, 21, 337; 1897, 23, 449; 1899, 30, 300; 1903, 42, 513, 629; Biltz, *ibid.* 1899, 29, 249; Robertson, Chem. Soc. Trans. 1903, 83, 1425; 1904, 85, 1617; 1905, 87, 1574; 1906, 89, 567). It should be noted that in cases also where the dissolved substance crystallises out along with the solvent, the depression of the freezing point is abnormally small, and the value of the molecular weight calculated therefrom is correspondingly high.

For the cryoscopic determination of the molecular weights of dissolved substances a method of moderate accuracy is sufficient, and an experiment may be carried out with a comparatively small quantity of liquid. The case is different with the problem of finding the exact depression of the freezing point for very dilute aqueous solutions—a problem to which much attention has been devoted because of its bearing on the theory of solution. It was early evident that the cryoscopic investigation of very dilute solutions involves special difficulties, for the discrepancies between the results obtained by different workers were very considerable. Thus the molecular depression for water, based on experiments with sucrose in which the actually observed depressions amounted only to about $0.05°$, was found by Arrhenius to be $20.2°$, by Raoult, $20.7°$; by Jones, $21.8°$; and by Loomis, $18.1°$, instead of the theoretical value, $18.6°$. Subsequent investigations (Nernst and Abegg, Zeitsch. physikal. Chem. 1894, 15, 681; Abegg, *ibid.* 1896, 20, 207; Wildermann, Phil. Mag. 1895, 40, 119; Proc. Roy. Soc. 1896, 251; Raoult, Zeitsch. physikal. Chem. 1898, 27, 617)

have made it clear what conditions must be fulfilled if the freezing point depression for a dilute aqueous solution is to be determined with certainty to 0·001°. It will be sufficient here to indicate these conditions briefly.

As regards the thermometer, it is essential that a telescope be used for reading the position of the mercury, and that the bulb of the instrument be kept at about 0° during the whole of a series of experiments. The influence of alterations in the atmospheric pressure cannot be neglected, for it appears that a difference of 1 mm. mercury has about the same effect on a Beckmann thermometer as a temperature change of 0·0002°. On similar grounds, the thermometer must be immersed always to the same depth in solvent and solutions. It should be mentioned here that platinum resistance thermometers have been used in accurate cryoscopic work instead of the Beckmann instruments (*see* Chrustchoff, Compt. rend. 1900, 131, 883; 1901, 133, 955; Bedford, Proc. Roy. Soc. A, 1910, 83, 454). The difference between the freezing points of solvent and solution has also been determined thermoelectrically (Hausrath, Ann. Physik. 1902, [iv.] 9, 522; Jahn Zeitsch. physikal. Chem. 1907, 59, 31; Flugel, *ibid.* 1912, 79, 577; Adams, J. Amer. Chem. Soc. 1915, 37, 481). •

The temperature of the cooling bath is a matter which has to be carefully considered, if the freezing point depression for a dilute solution is to be correctly determined. Suppose that in an experiment with the ordinary Beckmann apparatus the aqueous solution in the inner tube cools without freezing, it is obvious that the lowest temperature to which the solution can fall must be higher than that of the cooling bath, because of the heat conducted from the air to the solution through the thermometer, stirrer, and tube, and because of the heat generated by the stirring. This lowest temperature, which the contents of the freezing tube tend to assume when no freezing takes place, is known as the *convergence temperature.* The difference between the convergence temperature and the temperature of the cooling bath varies, of course, with each apparatus; it decreases as the facility for heat exchange between the solution and the external air is lessened, and as the rate of stirring is diminished. Suppose now that the solution under examination has become supercooled, and that it has reached the convergence temperature. The introduction of a crystal of the solid solvent at this stage initiates the freezing process; heat is liberated and the temperature of the solution rises. Inasmuch, however, as the solution is no longer at the convergence temperature, there is an influence at work tending to lower the temperature of the solution, so that the latter never reaches its true freezing point: the maximum position reached by the mercury is only what may be called the *apparent* freezing point of the solution. Similarly, when the freezing point of the solution lies below the convergence temperature, an apparent freezing point is observed which is somewhat higher than the true freezing point. In both cases, the apparent freezing point lies between the true freezing point and the convergence temperature. In view of these considerations, it is necessary, in cryoscopic work

of the most accurate kind, either to adjust the cooling bath so that the convergence temperature and the freezing point are practically the same, or to apply a correction to the apparent freezing point (*see* Raoult, *l.c.*; Nernst and Abegg, *l.c.*).

The freezing point of a solution is the temperature at which the solution and the solid solvent are in equilibrium, and in order that this equilibrium, and therefore the freezing point, may be well defined, it is essential that a considerable quantity of solid should be in contact with the solution. In the case of aqueous solutions, this has generally been effected by supercooling to the extent of 0·5° or 1·0°, and then introducing a crystal (*see* Walker and Robertson, Proc. Roy. Soc. Edin. 1903, 24, 363; Richards, J. Amer. Chem. Soc. 1903, 25, 291; Jahn, Zeitsch. physikal. Chem. 1904, 50, 129; Roth, *ibid.* 1912, 79, 601; Adams, J. Amer. Chem. Soc. 1915, 37, 481; compare also Prytz, Ann. Physik. 1902, [iv.] 7, 882). In this method of procedure, equilibrium between the two phases is very rapidly established and the concentration of the liquid is ascertained by an analysis made subsequently to the determination of the freezing point.

It has already been pointed out that the freezing point depression is proportional to the number of dissolved units. The cryoscopic method may therefore be employed, not only in the determination of the molecular weights of dissolved substances, but also in the study of the question whether in a particular case a change in the number of dissolved units takes place. It is found, for instance, that the freezing points of potassium iodide solutions are not appreciably affected by the addition of iodine, which shows that the iodine must combine with the units already present in the solution (*see* Le Blanc and Noyes, Zeitsch. physikal. Chem. 1890, 6, 385; Paternò and Peratoner, Gazz. chim. ital. 1890, 21, 110). The cryoscopic method may similarly be employed in following the course of a reaction between dissolved substances which involves a change in the number of units, as for instance, the inversion of sucrose (*see* Kahlenberg, Davis, and Fowler, J. Amer. Chem. Soc. 1899, 21, 1).

J. C. P.

CRYPTOPINE *v.* OPIUM.

CRYSOBERYL or **CHRISOBERYL** *v.* GLUCINUM.

CRYSTAL PONCEAU *v.* AZO- COLOURING MATTERS.

CRYSTAL VARNISH or **PAPER VARNISH** *v.* VARNISH.

CRYSTAL VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

CRYSTALLIN *v.* PROTEINS.

CRYSTALLISATION. Crystals are often produced during the concentration of liquors in evaporating pans. Hand or mechanical scrapers are used for removing these crystals continuously. Such crystals are generally too

impure for sale and are redissolved in sufficient hot water to produce a solution, which, after clarification by subsidence or filtration, will yield, in the crystallising pan, bright and marketable crystals. The temperature and concentration of the solution, to yield the best result, have to be determined for every substance. The mother liquor is run off and the crystals transferred to drainers or centrifugal machines to be dried before packing. In some instances, several repetitions of this treatment are made, and the crystals are washed with water or liquor after each treatment. The crystallising pans are made of materials which give the best economic result; either they resist the mother liquors or, if attacked, do not spoil the product by discolouration or too much impurity. Cast-iron tanks about 2 feet deep with bottoms sloping to the outlet and rounded corners, are common. Wooden tanks unlined or lined with sheet lead, zinc, tin, or other metal, are used largely. Some manufacturers suspend roughened strips of metal in the pans, to which the crystals adhere. For rapid production, crystallisation by repose is now giving place in many industries to crystallisation in motion. The crystallising vessels are provided with circulating blades or with compressed air jets, so that the crystals as they form are prevented from adhering to the sides of the vessel, but remain suspended in the liquor, which, on complete cooling, flows directly to the centrifugal machines for the separation of the mother liquor. These crystals are purer and more convenient to handle than those obtained by repose methods. In the case of deliquescent substances and also in those instances where the mother liquor is sufficiently pure to make it unnecessary to purify by crystallisation, the liquor is concentrated in film evaporators so that only sufficient water remains in it to form the crystal. The liquor produced is run into drums, and forms on cooling, a solid block of crystals In some works, the liquor is run into a jacketed worm conveyor so that the crystals which form, leave the apparatus in a loose state.

The capacity of crystallising plant can be determined from a knowledge of the physical data involved. When crystallising by repose methods the rate of evaporation of the solution is given very closely by the utility formula :

$$W = \left(\frac{p_e - p_d}{50}\right)^{1\cdot2}$$

where W is the weight of water in kilograms evaporated per hour per square metre of surface of the liquid, p_e is the vapour pressure of the solution in mm. of mercury at the temperature under consideration, and p_d is the pressure of the aqueous vapour in the atmosphere of the factory. If a draught with a velocity exceeding (say) 1 metre per second is produced in the crystallising room, the figure given by the above formula will be low, and should be multiplied by a factor which is approximately the square root of the velocity in metres per second.

If the mother liquor is run into the crystallising vessels hot, then the time of cooling and evaporation can be determined by a graphical integration of the rates of cooling from the surface of the vessel and cooling from evapora-

tion from the surface of the liquid at a series of temperatures.

Many solutions will not produce bright crystals at temperatures above 20° C. ; in such cases, propeller fans are most useful in keeping down the temperature and increasing the output.

Substances which form hard cemented masses on the cool surfaces of the crystallising vessels may be most satisfactorily treated in vacuum evaporators, where the crystals form on the surface and then drop to the bottom of the vessel, unless a stirrer be provided to keep them in suspension. This method is most useful when crystallising from volatile solvents.

Crystals of uniform size are also most efficiently produced in this way, since the rate of evaporation and the temperature can be perfectly regulated. A mother liquor of suitable strength is produced in the pan and allowed to cool to saturation temperature. The solution is then 'sown' with a suitable quantity of finely powdered substance, and the heating coils and vacuum pump set to work at such a rate as to maintain the temperature and produce the required amount of evaporation, the liquid being stirred continuously As soon as the crystals are known to have reached the required size, the mass is discharged through strainers and the mother liquor returned to form a portion of the next charge.   J .W. H

CUBA BLACK v. AZO- COLOURING MATTERS.

CUBEBS. *Cubebæ fructus*, B.P. The dried full-grown unripe fruits of *Piper Cubeba* (Linn. fil.).

CUBEBS CAMPHOR v. CAMPHORS.

CUBEBS, OIL OF, v. OILS, ESSENTIAL.

CUCUMBER. The fruit (really a berry) of *Cucumis sativus* (Linn.). König gives as the average composition :

Water	Nitrogenous matter	Fat	Sugar	Other carbo- hydrates	Fibre	Ash
95·36	1·09	0·11	1·12	1·09	0·78	0·45

According to Wittmann (1901), cucumbers contain about 0·2 p.c. of pentosans.

Heinze (Zeitsch. Nahr. Genussm. 1903, 6, 529) observed that large cucumbers contain a higher proportion of sugar than small ones, but less nitrogenous matter. He gives as the mean composition :

	Water	Pro- tein	Fat	Glu- cose	Cane sugar	Other carbohy- drates	Fibre	Ash
Small	96·6	0·81	0·09	0·00	0·10	1·44	0·58	0·34
Large	95·8	0·67	0·09	0·66	0·09	1·60	1·65	0·42

The ash of cucumbers contains :

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
51·7	4·2	7·0	4·5	0·8	13·1	5·7	4·3	9·2

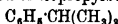   H. I.

CUDBEAR v. ARCHIL.

CULLEN EARTH or **COLOGNE EARTH** v. PIGMENTS.

CULLET v. GLASS.

CULM v. *Anthracite*, art. FUEL.

CUMENES. *Cumols.* The name *cumene,* originally applied to *iso*propylbenzene

$$C_6H_5 \cdot CH(CH_3)_2$$

to indicate its connection with *cumic acid,* from which it was obtained by distillation with lime, is frequently employed as a generic term to denote any of the isomeric benzene hydrocarbons of the formula C_9H_{12}. Theory predicts

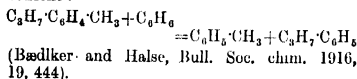the existence of eight of these, all of which have been found in coal-tar oil.

Propylbenzenes.

1. *Normal propylbenzene* (n- *cumene*)

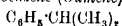$$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$$
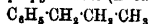
Present in coal tar oil in fraction boiling at 153°–157° (Schultz and Perl, Ber. 1909, 3602). By the action of sodium on a mixture of bromobenzene and propyl bromide in ethereal solution (Fittig, Schäffer and König, Annalen, 149, 324). By the action of aluminium chloride on trimethylene bromide, propylbenzene and diphenylpropane (sym.) are formed, the latter of which, on further treatment, yields propylbenzene and cumene (Bodroux, Compt. rend. 132, 155). From benzene, aluminium chloride and propyl bromide, when kept at 0° (Heise, Ber. 1891, 768; Genvresse, Bull. Soc. chim. 9, [3] 219). From benzyl chloride, $C_6H_5 \cdot CH_2Cl$ and zinc-ethyl (Paternò and Spiza, Ber. 10, 294). Liquid boiling at 159° (corr), sp.gr. 0·867 at 15°/15° (Perkin, Chem. Soc. Trans. 1900, 274). Yields benzoic acid on oxidation with chromic acid.

Cumene, together with toluene, may be obtained from cymene by demethylation by the action of aluminium chloride in presence of benzene :

$$C_3H_7 \cdot C_6H_4 \cdot CH_3 + C_6H_6$$
$$= C_6H_5 \cdot CH_3 + C_3H_7 \cdot C_6H_5$$

(Bædlker· and Halse, Bull. Soc. chim. 1916, 19, 444).

2. *Isopropylbenzene* (*Cumene*)

$$C_6H_5 \cdot CH(CH_3)_2$$

Present in American petroleum (Maberry and Dunn, Amer. Chem. J. 18, 215). By distilling cumic acid $C_6H_4[CH(CH_3)_2]CO_2H(1, 4)$ with lime or baryta (Gerhardt and Cahours, Ann. Chim. Phys. [3] 1, 87). From benzal chloride $C_6H_5 \cdot CHCl_2$ and zinc-methyl (Liebermann, Ber. 13, 46). Phenyl magnesium bromide reacts with acetone to give methylethenylbenzene, which, on hydrogenation, yields cumene (Tiffeneau, Compt. rend 134, 845). From benzene and either isopropyl bromide or normal propyl bromide in presence of aluminium bromide (Gustavson, Ber. 14, 1251) Liquid boiling at 152·5°–153° (corr.); sp.gr. 0·8727, 7·9°/4° (Perkin, Chem. Soc. Trans. 1900, 275). Yields benzoic acid on oxidation with chromic acid.

Methylethylbenzenes (*Ethyltoluenes*). The three methylethylbenzenes are obtained by the action of sodium on a mixture of ethyl bromide or iodide with the corresponding bromotoluenes (ortho-, meta-, or para-).

1. *o-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 2)$$
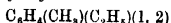
Liquid boiling at 158°–159° ; sp.gr. 0·8731 at 16°. Dilute nitric acid oxidises it to o-toluic acid $C_6H_4(CH_3)CO_2H(1, 2)$.

2. *m-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 3)$$
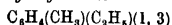
Liquid boiling at 158°–159° ; sp.gr. 0·869 at 20°. Chromic acid oxidises it to isophthalic acid $C_6H_4(CO_2H)_2(1, 3)$.

3. *p-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 4)$$

Liquid boiling at 161°·162° ; sp.gr. at 0·8652 at

21°. yields on oxidation p-toluic and terephthalic acids.

Trimethylbenzenes.

1. *Consecutive trimethylbenzene* (*Hemellitene* ; *Hemimellithene*) $C_6H_3(CH_3)_3(1, 2, 3)$. By heating the calcium salt of a-*isoduric* acid

$$C_6H_2(CH_3)_3CO_2H$$

with lime. Liquid boiling at 175° (Jacobsen, Ber. 15, 1857 ; 19, 2517).

2. *Unsymmetrical trimethylbenzene* (*pseudocumene*) $C_6H_3(CH_3)_3(1, 2, 4)$, occurs together with mesitylene in coal-tar (Beilstein and Kögler, Annalen, 137, 317), and is present in many petroleums (Poni, Chem. Zentr. 1906, i. 459). By the action of sodium on a mixture of either bromo-paraxylene or bromometaxylene with methyl iodide. In order to isolate it from coal tar, Armstrong recommends (Chem. News, 38, 5 ; Ber. 11, 1697) that the mixture of pseudocumene and mesitylene (v infra) boiling between 160° and 170°, obtained from coal tar by fractional distillation, should be converted by treatment with an equal volume of concentrated sulphuric acid into sulphonic acids. The mixture of sulphonic acids, which separates as an oily layer on carefully adding water to the sulphuric acid solution, is heated with concentrated hydrochloric acid in a sealed tube for 1 hour at 100°. In this way, the mesitylene sulphonic acid is decomposed, regenerating mesitylene, whilst the pseudocumenesulphonic acid is not attacked. After separating the mesitylene the pseudocumenesulphonic acid is precipitated from the hydrochloric acid solution by sulphuric acid, purified by recrystallisation from dilute sulphuric acid and finally decomposed by heating with hydrochloric acid at 140°-150°, when it breaks up into pseudocumene and sulphuric acid. Jacobsen (Ber. 9, 256) treats the mixture of sulphonic acids with barium or calcium carbonate, which removes the excess of sulphuric acid and converts the sulphonic acids into barium or calcium salts ; transforms these by double decomposition with sodium carbonate into sodium salts ; heats the latter with phosphorus pentachloride, with which they yield the sulphonic chlorides $C_9H_{11} \cdot SO_2Cl$; converts the chlorides into the sulphonamides

$$C_9H_{11}SO_2 \cdot NH_2$$
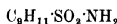
by the action of ammonia ; and separates the two isomeric sulphonamides by recrystallisation from alcohol, in which mesitylene sulphonamide is readily, pseudocumene sulphonamide only sparingly, soluble. The sulphonamides are then hydrolysed by heating with concentrated hydrochloric acid at 175°.

Another method proposed by Jacobsen (Annalen, 184, 199) is to separate the two sulphonic acids by fractional crystallisation ; pseudocumenesulphonic acid is soluble with difficulty in sulphuric acid and crystallises out. On heating to its melting-point (11C°) and passing in steam at a temperature of 250°, pure pseudocumene is obtained (see also Schultz and Herzfeld, Ber. 1909, 3602). Pseudocumene boils at 168·2°, and has sp.gr. 0·877 at 18° (Schultz and Herzfeld, l.c.). On oxidation with nitric acid, it yields two isomeric acids of the formula $C_6H_3(CH_3)_2CO_2H$—xylic acid and p-xylic acid

—and a small quantity of the isomeric methyl-isophthalic and methylterephthalic acids

$$C_6H_3(CH_3)(CO_2H)_2$$
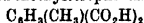
(Bentley and Perkin, Chem. Soc. Trans. 1897, 165).

3. *Symmetrical trimethylbenzene* (*Mesitylene*) $C_6H_3(CH_3)_3(1, 3, 5)$. In coal-tar oil, in fraction boiling at 157°–162° (Fittig and Wackenroder, Annalen, 151, 292 ; Schultz and Perl, Ber. 1909, 3602), and in American petroleum (Maberry and Dunn, Amer. Chem. J. 18, 215). By distilling acetone with sulphuric acid

$$3CO(CH_3)_2 = C_6H_3(CH_3)_3 + 3H_2O$$
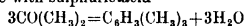
(Küster and Stollberg, Annalen, 278, 207 ; Meyer and Molz, Ber. 1896, 2831), or by dissolving allylene $CH_3 \cdot C \vdots CH$ in sulphuric acid and distilling with water $3CH_3 \cdot C \vdots CH = C_6H_3(CH_3)_3$ (Fittig and Schrohe, Ber. 8, 17). (On the isolation of mesitylene from coal tar and the method of separating it from pseudocumene, v. preceding paragraph.) Liquid boiling at 164·5° ; sp.gr. 0·8768 at 4°/4° (Perkin, Chem. Soc. Trans. 1896, 1193). Dilute nitric acid oxidises it to mesitylenic acid $C_6H_3(CH_3)_2CO_2H$ and uvitic acid $C_6H_3(CH_3)(CO_2H)_2$; with potassium permanganate it yields uvitic acid and trimesic acid $C_6H_3(CO_2H)_3(1, 3, 5)$.

CUMIDINES $C_9H_{13}N$. Of the sixteen isomeric cumidines which have hitherto been obtained, pseudo- and ψ-cumidine and mesidine are perhaps the most important. These bases are derivatives of pseudocumene and mesitylene respectively, the first of which is theoretically capable of yielding three isomeric ψ-cumidines, and the latter one cumidine only.

Pseudocumidine, *sym.-ψ-cumidine*

$$(CH_3)_3C_6H_2 \cdot NH_2[CH_3 : CH_3 : CH_3 : NH_2 = 1 : 2 : 4 : 5]$$

can be obtained by nitrating pseudocumene with fuming nitric acid in the cold, and reducing the nitro- compound (m.p. 71°) with tin and hydrochloric acid (Schaper, Zeitsch. chem. [2] 23, 1) The base is prepared technically by digesting xylidine hydrochloride with methyl alcohol in an autoclave at 280°–300°, converting the crude product into the nitrate, separating the sparingly soluble nitrates by means of a centrifugal machine, washing the product with water and finally treating with an alkali. The mixture of bases consisting of cumidines and xylidines is then fractionated, and the portion distilling between 225°–245° is allowed to crystallise, and finally freed from non-crystallisable bases by pressure (Aktiengesellschaft fur Anilin-fabrikation, D. R. P. 22265). The cumidine so obtained contains mesidine and other impurities (Hofmann, Ber. 17, 1912 ; Engel, *ibid.* 18, 2229), but consists chiefly of Schaper's pseudo-cumidine (*cf.* Hofmann, *ibid.* 15, 2895) which can be prepared in the pure state by digesting o-4-xylidine [$NH_2 : CH_3 : CH_3 = 1 : 3 : 4$] or para-xylidine with methyl alcohol under similar conditions (Nölting and Forel, *ibid.* 18, 2680).

Properties.—Pseudocumidine crystallises in large, lustrous prisms, melts at 63° (Hofmann), at 68° (Auwers, Ber. 18, 2661), and boils at 234°. It is insoluble in water, but readily soluble in alcohol. The nitrate is characterised by being very sparingly soluble in water. Its acetyl derivative crystallises in compact white needles, melts at 161° (Edler, *ibid.* 18, 629 ; Nölting and

Baumann), at 164° (Auwers) and boils above 360°. Pseudocumidine is used as a source of azo- dyes (D. R. PP. 3229, 1878 ; 22265, 1882).

as-ψ-cumidine [$CH_3 : CH_3 : CH_3 : NH_2 = 1 : 2 : 4 : 6$] has been prepared by Edler (*l.c.*). It melts at 36°.

ψ-**cumidine** [$CH_3 : CH_3 : CH_3 : NH_2 = 1 : 2 : 4 : 3$] is obtained by digesting o - 3 - xylidine hydrochloride [$NH_2 : CH_3 : CH_3 = 1 : 2 : 3$] with methyl alcohol in an autoclave at 300° (Nölting and Forel ; *cf.* Mayer, Ber. 20, 972). It boils at 240° (Nölting and Forel), 236° and does not solidify at −15° (Mayer). Its acetyl derivative melts at 186°.

Mesidine [$CH_3 : CH_3 : CH_3 : NH_2 = 1 : 3 : 5 : 2$] is obtained by treating mesitylene with nitric acid (sp.gr. 1·38) and reducing the nitro- derivative with tin and hydrochloric acid (Fittig and Storer, Annalen, 147, 3). It can also be prepared by digesting a-metaxylidine [$NH_2 : CH_3 : CH_3 = 1 : 2 : 4$] (Hofmann, Ber. 5, 715 ; 8, 61) or β-metaxylidine [$NH_2 : CH_3 : CH_3 = 1 : 2 : 6$] hydrochloride (Nölting and Forel) with methyl alcohol at 300°.

Properties.—Mesidine is a colourless liquid, which boils at 229°, and has a sp.gr. 0·9663. The acetyl derivative melts at 216° and crystallises in prisms.

Isocumidine [$CH_3 : CH_3 : CH_3 : NH_2 = 1 : 2 : 3 : 5$], prepared by digesting the hydrochloride of γ-metaxylidine

$$[NH_2 : CH_3 : CH_3 = 1 : 3 : 5]$$
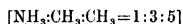
with methyl alcohol, at 300° (Nölting and Forel ; Limpach, Ber. 1888, 644), melts at 67°–68°, boils at 245°, and yields an acetyl derivative melting at 163°–164°.

Para-aminopropylbenzene, formed by heating aniline, propyl alcohol, and zinc chloride at 280° for 8 hours (Louis, Ber. 16, 105 ; Francksen, *ibid.* 17, 1221), boils at 224°–226°. The acetyl derivative melts at 87°.

Orthoamino*iso***propylbenzene**, - *o* - **cumidine**, formed by heating aminocumic acid with baryta (Filetti, Gazz. chim. ital. 13, 379 ; *cf.* Constam and Goldschmidt, Ber. 1888, 1158), boils at 213·5°–214·5° at 732 mm. The acetyl derivative melts at 72°.

Para-amino*iso***propylbenzene, cumidine,** formed by heating *iso*propyl alcohol, aniline, and zinc chloride at 260°–280° (Louis, Ber. 16, 111 ; *cf.* Nicholson, Annalen, 65, 58), boils at 216°–218°. The acetyl derivative melts at 102°–102·5°. By oxidation with sodium chlorate and potassium ferrocyanide in hydrochloric acid solution, cumidine yields a dyestuff of the aniline black series (Kirptischnikow, Chem. Zentr. 1906, i. 829). By treatment with cyanogen chloride in pyridine solution, condensation is effected and a dyestuff is produced (König, D. R. P. 155782 ; Chem. Zentr. 1904, ii. 1557).

Ethylorthotoluidine, prepared by treating orthotoluidine in ethyl alcohol with zinc chloride at 270° (Benz, Ber. 15, 1650), boils at 229°–230°. The acetyl derivative melts at 105°–105·5°, and boils at 313°–315°.

CUMIDINE RED *v.* AZO- COLOURING MATTERS.

CUMIN, OIL OF, *v.* OILS, ESSENTIAL.

CUPFERRON *v.* HYDROXYLAMINE.

CUPRATION. Copper albuminate.

CUPREINE *v.* CINCHONA ALKALOIDS.

CUPRENE (C_7H_8)$_x$. A yellow substance

obtained by passing acetylene over reduced copper heated above 180°, and treating the brown solid so formed repeatedly with acetylene until no further change occurs.

CUPRI-ADEPTOL. Copper m-phenol sulphonate.

CUPRISIN. Trade name for a preparation of cupric cyanide and potassium cyanide, used for the treatment of trachoma.

CUPRITE. Native cuprous oxide, Cu_2O, crystallising in the cubic system. Brilliant, transparent crystals of a ruby-red colour (hence the name ruby-copper-ore) are not uncommon; sp.gr. 6·0. In the variety called *chalcotrichite*, the crystals are capillary in form, being enormously elongated in the direction of one of the cubic edges, and are loosely matted together in plush-like masses Another variety, known as *tile-ore* (Ger. *Ziegelerz*), is earthy or compact and of a brick-red or brownish colour; it consists of an intimate mixture of cuprite and limonite, and has resulted from the alteration of copper-pyrites Cuprite is sometimes of importance as an ore in the upper oxidised portions of copper veins. L. J. S.

CUPROCITROL. Trade name for copper citrate.

CUPROL. A compound of nucleinic acid and copper.

CUPRONICKEL *v.* NICKEL.

CUPROSILICON, *Cuprous silicide* (*v.* COPPER)

CURARA. *Curare, Urari, Woorari, Woorah, Woorara.* Curara is the arrow poison of those tribes of South American Indians which inhabit the districts lying between the Amazon and the Orinoco. It was first brought to Europe by Sir Walter Raleigh, in 1595, and from that time to this its origin and preparation have been much discussed by travellers and botanists. A summary of the earlier observations of La Condamine, A. v. Humboldt and Bonpland, Waterton, Schomburgk, Castelnau, Weddell, Thiron, Jobert, Crévaux, and others is given by Planchon (Pharm. J. [3] 11, 469, 491, 529, 589, 693, and 754). It is shown that curara is an aqueous extract of a mixture of many plants, one of which is always a species of *Strychnos*, and gives to it the chief toxic power, whilst the remainder contribute those other qualities which render the extract suitable for the tipping of arrow heads. The method of preparation adopted by one tribe of Indians is described by Schomburgk (*ibid.* [3] 10, 646). The product differs somewhat with the locality in which it is prepared. Planchon distinguishes four varieties: the curara of the Orinoco, of the Upper Amazon, of French Guiana, and of British Guiana. The chief active ingredient in the preparation of the first is a *Strychnos* plant, closely allied to Schomburgk's *S. toxifera* (J. Pharm. Chim. [5] 5, 20), of the second, *S. Castelnæi* (Weddell), of the third, *S. Crevauxiana* (Baill.), and of the fourth, *S. toxifera* (Schomb.).

As seen in Europe, curara is a brown to black, nearly solid, or even brittle, extract. It has a bitter taste, and in its poisonous action it is related, though opposed, to strychnine. In medicine, it has been occasionally employed in the treatment of tetanus and hydrophobia, but it is not included in any pharmacopœia. Great care is necessary in its administration, and the solution should first be tested on animals.

For the earlier chemical investigations of curara, *see* Flückiger (Arch. Pharm. 1890, 228, 78). Our present knowledge is mainly due to Boehm (Chem. Zentr. 1895, ii. 1084; 1897, ii. 1078; Arch. Pharm. 1898, 235, 660), who showed that the alkaloids of curara can be divided into two classes: (1) compounds similar to curine, partly crystalline and partly amorphous, soluble in water with difficulty and precipitated from solution by ammonia, in which the characteristic toxic effect of curara is shown very slightly or not at all; (2) amorphous yellowish-red substances easily soluble in water as curarine, not precipitated by ammonia, and showing the most marked toxic action. Of most specimens of curara, about 70–90 p.c. is soluble in tepid water; sometimes, however, scarcely more than half is soluble. Para curara, which is imported in bamboo tubes and is the variety now usually met with in commerce, contains about 11–14 p.c. water, 12 p.c. ash, 12–15 p.c. *curine* $C_{18}H_{19}O_3N$, which is isolated by extracting the raw material with water, precipitating by aqueous ammonia and extracting with alcohol. It melts at 212°, and is obtained in crystals from benzene or alcohol with one molecule of the solvent or from methyl alcohol without alcohol of crystallisation. *Tubo-curarine (paracurarine)* $C_{19}H_{21}O_4N$ was obtained as a reddish-yellow substance which forms about 9–11 p.c. of raw curara. It is not identical with the previously known curarine, isolated from calabash curara. The latter kind, which was sent over from the Orinoco *via* Venezuela in small gourds, used to be the common variety, but is now seldom met with; it is much superior to tube curare, and seems to be derived from *Strychnos toxifera.* Earlier investigations, as a rule, refer to this. The active principle, *curarine* $C_{19}H_{26}ON_2$ (?), consists of hard glistening garnet-red laminæ, decomposing and giving off a smell of trimethylamine when heated to 150°. A minute quantity of a second alkaloid was found to be present.

A third variety of curara, from the Upper Amazon, occurs in the market in small jars of unburnt clay. This differs widely in respect to active principles from the other varieties. The following substances have been extracted from it: *protocurine* $C_{20}H_{23}O_4N$, colourless needles, which turn brown at 160° and melt, with decomposition, at 306°; *protocuridine* $C_{19}H_{21}O_3N$, colourless prismatic crystals, m.p. 274°–276°; and *protocurarine* $C_{19}H_{23}O_4N$ (?), an amorphous red powder, more poisonous than the other curarines.

The inert, or slightly active, curines appear to be tertiary bases, the curarines are quaternary ammonium bases, and in this connection it is noteworthy that, according to Crum Brown and Fraser (Proc. Roy. Soc. Edinburgh, 1869, 560), nearly all ammonium bases paralyse motor nerve endings and have a curare-like effect. In the case of curine and tubo-curarine, at least, there seems to be a close chemical relationship; both appear to be derivatives of methoxylated quinoline. Curine methiodide produces the typical curare effect and resembles tubocurarine. The colour reactions of curarine indicate a relationship to strychnine. Pure curarine is extremely active; $\frac{1}{10}-\frac{1}{20}$ mg. injected will paralyse a frog; given by the

mouth it is inactive. It paralyses the motor nerve endings, but, even in large doses, leaves other tissues unaffected. Hence it is much employed in physiological research (*cf. e.g.* Edmunds and Roth, Amer. J. Physiol. 1908, 23, 28, 46). G. B.

CURCAS OIL, purging nut oil, physic nut oil (*Oleum infernale*), is obtained from the seeds of *Jatropha curcas* (Linn.), (purging nut '), by hot expression. The seeds consist of 66 p.c. of kernels and 34 p.c. of husks. From the former there is obtained by extraction with ether 52 p.c. of oil of a pale colour, becoming yellow, with a reddish tint, on exposure to the air. Characteristic of the oil is its unpleasant odour, which assists in distinguishing curcas oil from other oils. Most prominent are the strong purgative properties of the oil, which are much more pronounced than those of castor oil. It may be distinguished from castor oil by its sparing solubility in alcohol, and ready solubility in petroleum spirit. The oil belongs to the semi-drying oils ; its liquid fatty acids consist of about equal proportions of oleic and linolic acids, as ascertained by the relative quantities of their oxidation products (viz. dihydroxy-stearic and tetrahydroxystearic acids). This oil is stated by Bouis to contain *isocetic* acid, but the existence of this acid is doubtful.

The recorded values show considerable variations, but genuine expressed oil has sp gr. 0·9204–0·9205 at 15·5° ; saponification value, 192–193 ; iodine value, 98–100 ; and acetyl value, 7·5–10.

In addition to its use as a medicine, curcas oil is also used in the manufacture of soap, and to a limited extent for burning.

Nearly related to the above-described oil are the oils obtained from the seeds of *Jatropha oligandra* (Mull.) and *J. multifida* (Linn.).

J. L.

CURCUMEÏNE *v.* Azo- colouring matters.

CURCUMIN *v.* Turmeric.

CURCUMINES *v.* Azo- colouring matters.

CURCUPHENINE *v.* Azo-colouring matters

CURINE *v.* Curara.

CUSCOHYGRINE *v.* Cocaine and the Coca alkaloids.

CUSPARIA BARK. *Angostura bark ; Carony bark. (Ecorce d'Angusture,* Fr. ; *Angostura-Rinde,* Ger.) The bark of the *Cusparia febrifuga* (Hiemb.) or *Galipea cusparia* (St. Hilaire), a tree inhabiting the mountain districts drained by the Orinoco (*cf.* Bentl. a. Trim. 43). Confusion has sometimes occurred between cusparia and nux vomica bark. The two barks may, however, be readily distinguished by treatment with a drop of nitric acid, which either deepens the colour of the cusparia or gives it a bluish shade, while nux vomica, similarly treated, exhibits a blood-red colour. Several other barks have, from time to time, been substituted for true angostura. (For these, and the mode of detecting them, *v.* Pereira (Mat. Med. 3rd. ed. 2, 1915) ; Maisch (Amer. J. Pharm. 1874, 50) ; Cazeneuve (Rép. de Pharm. 1874, 261) ; Oberlin and Schlagdenhauffen (Pharm. Zeit. 1878, 853).) For the bark of *Esenbeckia febrifuga,* which enters commerce under the name of angostura bark, *see* Hartwich and Gamper (Arch. Pharm. 238, 568). Cusparia

bark contains about four alkaloids, a little ethereal oil, a bitter principle, and a glucoside. Of total alkaloids there is 1·8 p.c. free and 0·6 p.c. in a combined state. By far the most abundant alkaloids are *cusparine* and *galipine,* discovered by Körner and Böhringer (Gazz. chim. ital. 1883, 13, 363). They are removed from the ethereal percolate of the bark by shaking with 20 p.c. acetic acid, which leaves small quantities of other bases behind. The separation of cusparine from galipine is effected by fractional crystallisation of the free bases, from ligroin, but principally by conversion into the oxalates ; cusparine oxalate is very little soluble in water, while galipine oxalate remains in solution (Tröger and Kroseberg, Arch. Pharm. 1912, 250, 494).

Galipine $C_{20}H_{21}O_3N$ forms colourless needles, m.p. 115° ; when pure the salts are colourless. Oxidation with permanganate yields veratric and methoxyquinoline carboxylic acids, whence Tröger and Kroseberg have suggested the following constitution :
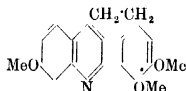
Cusparine has, according to Tröger and Beck (Arch. Pharm. 1913, 251, 246), the composition $C_{19}H_{17}O_3N$, and not $C_{20}H_{19}O_3N$, as previously supposed. It is probably trimorphous, and may melt at 90°–91°, or at 110°–122°. Its salts, and particularly the oxalate, are sparingly soluble, and hence it is the easiest of the angostura alkaloids to isolate. Sulphuric acid gives a dull-red, rapidly changing to cherry-red, Frohde's reagent a deep-blue, colouration. On melting its salts with organic acids, it changes to *pyrocusparine* $C_{18}H_{15}O_3N$, m.p. 255°, which base gives well-crystallised salts. Like galipine, cusparine seems to be a quinoline derivative (Tröger and Beck). It is a tertiary base, and contains one methoxyl group. As protocatechuic acid is obtained by potash fusion, it is conceivable that it contains a methylenedioxy group instead of the two methoxy groups of galipine, which would be in accordance with the empirical formula. *Cusparine* $C_{18}H_{19}O_2N$, according to Tröger and Runne (Arch. Pharm. 1911, 249, 174), is extracted by light petroleum from the amorphous bases left after crystallisation of cusparine and galipine. It melts at 56°, distils almost without decomposition, contains two methoxy groups, and yields quinoline on zinc-dust distillation. Tröger and Runne also describe *galipoidine* $C_{19}H_{15}O_4N$, m.p. 233°, and Tröger and Beck (*l.c.*) yet another alkaloid $C_{16}H_{13}O_5N$ (?), m.p. 186°. Cusparidine and galipidine of Beckurts and Nehring are, according to Tröger and Kroseberg, merely mixtures of cusparine and galipine. Other papers on angostura alkaloids are by Tröger and Müller (Arch. Pharm. 1910, 248, 1 ; 1914, 252, 459), by Beckurts and Nehring (Arch. Pharm. 1891, 229, 591),·and by Beckurts and Frerichs (Arch. Pharm. 1905, 243, 470).

The *essential oil* (from *Cusparia trifoliata,* Engl.) is described in Schimmel and Co.'s Semi-Annual Report, April, 1913. The yield was

1·03 p.c. of the bark ; D_5^{15} 0·9285 ; $a_D^{20}-7·32°$; n_D^{20} 1·50744 ; colour, pale brown ; acid number, 1·8 ; ester number, 5·5 ; acetyl number, 35·7 ; the oil is not completely soluble even in 9 volumes of 90 p.c. alcohol.

Angosturin $C_9H_{12}O_5$, m.p. 58°, is a crystalline bitter principle, readily soluble in water and in alcohol, but not in ether (Beckurts and Nehring).

Angostura bark is a constituent of 'Angostura bitters,' and is used in medicine as a tonic in derangements of the alimentary canal, but it is not included in the B.P. nor in the U.S.P.

G. B.

CUSSO, KOUSSO, *v.* Kosin, art. RESINS.

CUSYLOL. Trade name for soluble copper citrate.

CUTCH. Considerable quantities of cutch are now prepared in Burma. It is obtained from the *Acacia Catechu*, the trees being felled while green, the bark taken off, and the timber chopped up and boiled in large cauldrons. The resultant liquid is drained off, and solidifies as it cools. In the better qualities of cutch only the heart-wood of the tree is utilised. Cutch is brought to the market in several forms, the three principal ones being : (1) tablets—small rectangular blocks weighing from 1 to 2 lbs. ; (2) blocks—more or less square blocks weighing from 28 to 56 lbs. ; (3) baskets—a soft cutch of a thick consistency. Tablet cutch is the best quality, and basket cutch the lowest. Block and basket cutch usually contain more impurities than tablet cutch. On arrival in Rangoon the cutch is packed in wooden cases (usually containing 1 cwt. net), and is then ready for export.

Cutch trees are found throughout the whole of Burma, but the principal producing districts are Prome, Thayetmo, Myingyan, Minbu, Pegu, Yamethin, and Pyinmana.

Cutch is used largely as a dye, and for tanning, and as a preservative, especially for preserving fishing nets and sails. *See also* CATECHU.

CYANACETIC ACID *v.* MALONIC ACID.

CYANELLAGIC ACID. Cyanellagic acid $C_{14}H_8O_{10}$ is prepared by heating ellagic or flavellagic acid with 100 p.c. sulphuric acid at 185°–230° (Perkin, Chem. Soc. Proc. 22, 114), or with arsenic and sulphuric acids at 130°. It crystallises from pyridine in small yellow prismatic needles, and is soluble in strong alkaline solutions with a green-yellow tint, changing to deep blue on dilution. The hexa-acetyl derivative $C_{14}O_{10}(C_2H_3O_6)$, forms colourless needles, melts at 330°–332°, and the hexabenzoyl compound, colourless needles, m.p. 343°–345°. Cyanellagic acid is most probably dihydroxyellagic acid, and in this case possesses the following constitution :—
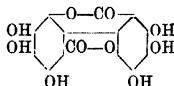
It dyes mordanted fabrics more readily than ellagic acid. A. G. P.

CYANIDES. Compounds of the radical cyanogen CN. The history of the cyanid

industry begins with the discovery of Prussian blue by Diesbach in 1704 (H. Kopp, Geschichte der Chemie, 4, 369). While attempting to make Florentine lake by precipitating a mixture of cochineal infusion, alum, and ferrous sulphate with an alkali, he obtained a blue colour. The alkali used was potash, over which Dippel had distilled his animal oil, and Dippel recognised in this the source of the blue colouring matter. The new blue very quickly came into use in place of ultramarine, and in 1710 it was sold at one-tenth the price of the latter. The method of manufacture was a secret until 1724, when Woodward showed that the blue could be prepared by calcining blood with potassium carbonate and then treating the aqueous extract [1] with ferrous sulphate and alum, the greenish precipitate so obtained yielding Prussian blue when treated with hydrochloric acid.

This, in its essential features, was the method of manufacture which supplied the world's requirements of cyanogen compounds for nearly 150 years.

Macquer, in 1752, showed that alum is not required, and that Prussian blue, when boiled with an alkali, yields ferric hydroxide and a soluble salt from which the blue can be regenerated. This salt, potassium ferrocyanide, was first obtained in the crystalline form by Sage in 1772.

The brilliant researches of Scheele, 1782–3 (Chemical Essays, London, 1786), Berthollet, 1790 (Ann. Chim. Phys. 1790, 1, 30), and of Gay Lussac, 1815 (ibid. 1815, 95, 156), in the course of which the relationships of the ferrocyanides, hydrocyanic acid, cyanogen, and many of their derivatives were discovered, laid a firm scientific foundation for the industry.

Prussian blue was manufactured in Great Britain in 1770 by Bramwell & Co. of Newcastle ; it sold then at 2 guineas per lb. ; the price had fallen in 1815 to 10s. 6d., in 1820 to 2s. 6d., and in 1850 to 1s. 9d. Crystallised potassium ferrocyanide was first known in commerce about 1825, the price being 5s. per lb., although a solution had been sold previously (Graham, Reports of Juries, Exhib. of 1851, 1, 95).

The conversion of potassium ferrocyanide into potassium cyanide by fusion with potassium carbonate, was first described by F. and E. Rodgers in 1834 (Phil. Mag. 1834 [3] 4, 91), but the simple cyanides were not used in any considerable quantity until the process of electroplating with gold and silver, from a cyanide solution, was discovered by J. R. and H. Elkington in 1840 (Eng. Pat. 8447, of 1840).

An interesting application of potassium ferricyanide was discovered by Sir J. Herschel in 1842 (Phil. Trans. 1842). Paper, treated with a solution containing ferric ammonium citrate and potassium ferricyanide, becomes blue when exposed to light, owing to the reduction of the ferric salt and consequent formation of Prussian blue. Paper sensitised in this way is used for the reproduction of engineering drawings.

A very remarkable attempt was made by Possoz and Boissière in the year 1843, to manufacture cyanides from atmospheric nitrogen ;

[1] *Lixivium sanguinis* or blood-lye, whence the German name of potassium ferrocyanide, '*blutlaugensalz.*'

this is described under the heading POTASSIUM CYANIDE.

The year 1860 witnessed three important developments in the cyanide industry. Gautier-Bouchard (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63) began to produce prussiate from the spent oxide of the Paris gas works. A. Gélis (Eng. Pat. 1816, of 1860) synthesised it from carbon disulphide and ammonia; and Margueritte and de Sour-deval (Eng. Pat. 1171, of 1860) attacked the problem of the fixation of atmospheric nitrogen by means of barium oxide and carbon.

The existence of cyanogen compounds in coal gas was known in 1843, and possibly still earlier. E. Jacquemyns (Annalen, 1843, 46, 236), whose attention was drawn to them by H. Rose, says that he found none in gas lime, but obtained 0·75 gram of Prussian blue per litre from ammonia liquor. The purification of coal gas by means of iron oxide was introduced in 1847. Owing to the repeated use of the same quantity of oxide, the cyanogen compounds accumulate in it in a relatively concentrated form, and it was therefore naturally the first gas works product to be used in their manu-facture. Prussian blue, made from spent oxide, was exhibited by Gauthier-Bouchard at the London Exhibition of 1862.

Both the process of Gélis and that of Mar-gueritte and de Sourdeval were soon abandoned by their inventors; the recovery of cyanides from spent oxide, on the other hand, developed fairly rapidly, and, according to Dupré (Journ. für Gasbeleuchtung, 1884, 885), there were, in 1884, 10 works making prussiate by this means.

The competition of the gas works ferrocy-anide, the increasing cost of nitrogenous organic matters (which were being more and more used as fertilisers), and the diminished use of Prussian blue due to the competition of blue colouring matters derived from coal tar, led to the dis-appearance of the old process in Europe about this time.

In the United States of America, it appears to have held its own somewhat longer; the returns of the U.S. Census for 1900 (Bulletin No. 210, 31, 1902) show 18 works engaged in the manufacture of cyanides with a joint annual production of 2752 tons of yellow prussiate, almost entirely made from hoofs, horns, and scrap leather, only 1200 tons of spent oxide having been used.

Between 1875 and 1885, the sulphocyanides, especially the tin and aluminium salts, appear to have been used in calico printing instead of the acetates (Bertelsmann, Die Technologie der Cyanverbindungen, 303), and Gélis' synthesis was taken up and improved by Günzburg and Tcherniac (Eng. Pat. 1148, of 1878; 1359, of 1879; 1261, of 1881), but without financial success.

In 1887, J. S. MacArthur, R. W. and W. Forrest (Eng. Pat. 14174, Oct. 19, 1887; 10223, of 1888) patented their process for the extraction of gold and silver from their ores by means of a dilute solution of a cyanide. The process was carried out by allowing a solution containing 0·25 p.c. or less of potassium cyanide to perco-late through the ore, which was usually ground to pass a sieve with 40 or 60 holes to the linear

inch. The gold is dissolved in the form of potassium aurocyanide, and is recovered from the solution by passing it through a mass of zinc shavings. The process was first put into practice at Karangahake, New Zealand, in 1889, and near Johannesburg, Transvaal, in 1890. The success of these installations led to a very rapid adoption of the process in all the gold-producing countries of the world.

Prior to the introduction of this process, the cyanide industry was quite a small one. The world's consumption of potassium cyanide (produced exclusively from ferrocyanide by the Rodgers process) (F. Roessler, V. Internationaler Kongress für Angewandte Chemie, Berlin, 1903, 1, 638) did not exceed 50–70 tons per annum (G. Beilby, J. Soc. Chem. Ind. 1898, 134) and that of yellow prussiate was probably under rather than over 5000 tons (worth together about 325,000l.).

Ten years later, just before the Transvaal War, the European production of potassium cyanide was estimated by Beilby (V. Inter. Kongress Angew. Chem. Berlin, 1903, 1, 630) as 5500 tons, adding the American production of about 1000 tons (U.S. Census Bulletin, No. 210, 31, 1902), we arrive at a total production of 6500 tons.

The increased quantities of potassium cyanide required by the gold-mines were at first supplied by fusing potassium ferrocyanide with potassium carbonate, and very soon afterwards by E. Erlenmeyer's process (Ber. 1876, 1840), in which dry prussiate and metallic sodium are used : $K_4Fe(CN)_6 + 2Na = 2NaCN + 4KCN + Fe$. Synthetic processes producing cyanide direct without the intervention of prussiate, were also proposed in great numbers. The approximate numbers of patents connected with cyanide manufacture applied for were : 1889–1898, 104 ; 1899–1908, 129 ; 1909–1917, 106. The principal processes which have been worked with some measure of success, are :—

Process.	Where worked.	Began pro-duction in
Siepermann.	Stassfurt, Germany.	1892
Beilby.	Glasgow, Scotland	1892
British Cyanides Co.	Oldbury, England.	1895
Raschen.	Runcorn, England.	1898
Readman.	Leven, Scotland.	1899
Castner.	Germany, Scotland, U.S.A.	1899–1900
Bueb ('Schlempe').	Dessau, Germany.	1902

These, and others, are described fully below.

The recovery of cyanides from the products of distillation of coal was also improved by the introduction of special cyanide scrubbers during the decade 1890–1900 ; whereas the iron oxide purifiers had yielded but little more than one-half of the cyanogen in a useful form, the newer processes give an almost quantitative recovery.

About the year 1900 the fruit trees of Cali-fornia and the Southern States of America were threatened with extermination by a parasitic scale. The investigations of the Experiment Stations of the U.S. Department of Agriculture showed that this could be killed without injury to the trees by fumigation with hydrocyanic acid. The method, which was introduced

about 1903, is now very widely used, both in the United States of America and in other countries. It has also been extended in other directions, such as killing insects in hot-houses, and freeing railway carriages and houses from vermin (in South Africa). Details will be found under the heading *Hydrocyanic acid*. Statistics collected by George P. Gray show that the consumption of sodium cyanide for fumigating citrus trees during 1916 in the State of California alone exceeded 1300 tons (J. Ind. Eng. Chem. 10, 301, 1918).

Another application which may be mentioned is in case-hardening iron; immersion in fused cyanide produces a very hard skin on mild steel, and both cyanides and ferrocyanides have long been used for this purpose in ordinary workshop practice. According to J. E. Bucher (J. Ind. Eng. Chem. 9, 236, 1917), the reversible reaction $2NaCN \rightleftharpoons 2Na + 2C + N_2$ takes place in presence of iron; if pure iron is heated with sodium cyanide the latter is decomposed and the carbon combines with the iron; if, on the other hand, carbonised iron is heated with sodium and nitrogen, the carbon is removed from it, and cyanide formed.

Potassium cyanide, as used in electroplating, was a material having the appearance of unglazed porcelain, and containing from 30 to 70 p.c. of KCN, together with large quantities of carbonate and cyanate. The material supplied to the gold-mines in the early days of the gold-extracting process was a black mass containing some 75 p.c. of KCN, and all the iron and carbon liberated by the decomposition of the ferrocyanide. This was replaced by the pure white crystalline product of the Erlenmeyer process, which contained about 2 molecules of KCN to 1 molecule of NaCN, the cyanogen content being about 40 p.c., equivalent to 98-100 p.c. of KCN. The earlier produce of the Beilby process was in the form of cakes, which were coloured black by a small percentage of charcoal. Later, by filtration of the molten cyanide, the charcoal was removed, and the product was white or pale grey, and free from insoluble impurities. Shortly after the introduction of the Castner process, in 1900, solid cakes of pure white crystalline sodium cyanide, containing 97 p.c. to 98 p.c. of NaCN (equivalent to 129-130 p.c. of KCN), became an article of commerce, and this is at present the form in which the greater part of the cyanide employed in gold-extracting is used. Sodium cyanide, obtained by the evaporation of aqueous solutions, as in the Readman and 'Schlempe' processes, is compressed into briquettes, which contain about 90 p.c. of NaCN.

Potassium ferrocyanide has also been replaced to a very large extent by the sodium salt which is quite easily prepared by the more recent methods of extracting the hydrocyanic acid from coal gas by special cyanogen washers.

The rapid rate of increase in the world's consumption of cyanide which followed the introduction of the gold-extracting process has not been maintained. Since 1909 the annual value of the world's gold output has been almost stationary at a little more than 90,000,000*l*., and improvements in the process of extraction have everywhere tended to diminish the quantity of cyanide needed to produce this. On the Rand, where this tendency seems to have almost reached a limit, the average consumption of cyanide is 0·4 lb. KCN per ton of ore treated (H. A. White, J. Chem. Met. and Min. Soc. S. Africa, 1915, 16, 24). Increased use in the treatment of silver ores (much delayed, however, by political troubles in Mexico) and in agriculture have kept the world's consumption from 1910 to 1920 approximately constant at, in round figures, 20,000 tons per annum. In 1912 and 1913 Germany exported 6700 tons per annum (The Mineral Industry, 1917, 25, 882). The deficit caused by the cessation of these exports on the outbreak of war in 1914 has been covered by increased production in Great Britain; a temporary shortage in the United States was soon overtaken by the American makers.

Manufacture of Potassium and Sodium Ferrocyanides.—(1) From nitrogenous organic matter.

The method of manufacture from nitrogenous organic matter is now only of historical interest.

The sources of nitrogen were horn, dried blood, hair, waste wool, and feathers (15-17 p.c. N), woollen rags (10-16 p.c. N), pigs' bristles (9-10 p.c. N), and old leather (4·5-7 p.c. N). These materials were sometimes charred before use, about 80 p.c. of the nitrogen being driven off in the form of ammonia, hydrocyanic acid, and a complicated mixture of nitriles and organic bases.

The process was carried out at first in pear-shaped, cast-iron muffles, which were replaced later by reverberatory furnaces, the beds of which were formed of cast-iron pans, 5 feet long, 3 feet wide, 4 inches deep, and about 2 inches thick. A charge of 2 cwt. of potash (usually made up of 2 parts of the 'blue salt' recovered in a later stage of the process, and 1 part of fresh potash) was put into the pan and fused with 18-20 lbs. of iron turnings; 2 cwt. of the dry nitrogenous materials were then stirred in gradually (2·5 to 3 cwt. of charred material could be added without making the mass too pasty). The temperature was then raised in order to complete the reaction, and the melt ladled out into iron moulds. After solidification, it was broken up and digested for 24 hours with water at 50°-60°, and finally extracted completely with boiling water. The solution obtained contained potassium ferrocyanide, sulphocyanide, carbonate and sulphide. It was evaporated to sp.gr. 1·28, and allowed to crystallise. Further evaporation yielded a second crop of impure crystals, the mother liquor of which was evaporated to dryness, leaving a mixture of potassium carbonate and sulphide, known as 'blue salt' which was returned to the fusion pan.

The black insoluble residue left from the extraction of the 'metal,' as the product of the fusion, was called, contained considerable quantities of potassium, mainly in the form of potassium ferrous sulphide and of double potassium, calcium, and aluminium silicates.

The quantity of 'metal' produced was very little greater than the weight of potash used, and 4 charges were put through in 24 hours, but practice varied considerably: C. Karmrodt (Wagner's Jahresber. 1857, 3, 139) speaks of

6 charges of 500 lbs. each as the normal output of a pan in 24 hours.

The yield of ferrocyanide was seldom more than 20 p.c. of the quantity theoretically obtainable from the nitrogen in the materials used when they were not previously charred. Using charred materials, as much as 57 p.c. of the remaining nitrogen was converted into ferrocyanide, corresponding with a yield of about 12 p.c. on the nitrogen originally present.

The quantity and composition of the black residues varied greatly with the kind of organic matter used. The main constituents were carbon (4–9 p.c.), ferrous sulphide, iron, and inorganic substances derived from the ash of the animal matters and adhering dirt, the principal being silica, lime, alumina, and phosphoric acid. The quantity of potassium combined with these substances in an insoluble form was considerable. According to Karmrodt (Wagner's Jahresber. 1857, 3, 139), 100 parts of ‘ metal ’ made (1) from horn gave 18·7 p.c. of dry residue, containing 12·2 p.c. of K_2O ; (2) from rags, 28·3 p.c. of residues, with 16·7 p.c. K_2O ; (3) from leather, 35·1 p.c. of residue, with 10·2 p.c. K_2O. These quantities represent about 4½, 9, and 7 p.c. of the potassium contained in the original charge, and since only some 10 p.c. of this is converted into ferrocyanide at each operation (R. Brunquell, Wagner's Jahresber. 2, 102, 1856), the loss of potash in the residues appears to have been from 45 to 90 p.c. of that usefully employed. Potash was also carried away with the flue gases. The iron pans survived several hundred operations.

The theory of the process was first given by Liebig (Annalen, 1841, 38, 20). Scheele (Chemical Essays, London, 1786 ; reprinted 1901) had already shown that *lixivium sanguinis* is essentially a solution of potassium cyanide and that the addition of a ferrous compound is necessary to convert it into prussiate. Liebig confirmed this by extracting the ‘ metal ’ with alcohol, which dissolves out potassium cyanide, leaving a residue from which no ferrocyanide can be obtained. He attributed the formation of the cyanide partly to the action of ammonia (formed by destructive distillation of the organic matter) on carbon, $C + NH_3 = HCN + H_2$, and partly to the action of potassium on the nitrogenous residue of carbon. It may be remarked that the temperature of the fusion could not have exceeded 1000°, since cast iron melts about 1100°, and the pans withstood some hundreds of fusions. The temperature, too, was lowered by the addition of the organic matter, occasionally sufficiently to cause the charge to solidify, so that the reaction between ammonia and carbon, which requires a temperature of about 1000°, could not have occurred to any great extent. The direct action of ammonia on potassium carbonate would, however, take place, although, the ammonia being evolved on the surface of the mass, the conditions were not favourable to it. As to the second of Liebig's reactions, the writer has found that potassium is not formed in appreciable quantity from a mixture of charcoal and potassium carbonate below about 1200°, certainly not at 1000°, so that the greater part of the cyanide must have been formed by the action of potassium carbonate itself on the unknown carbon-nitrogen com-

pounds contained in the charred organic matter. That cyanide may be formed in this way is indicated by the fact that carbazol, when heated to redness with caustic potash, yields considerable quantities of it (G. Kraemer, Eng. Pat. 16529, of 1894). The rôle of sulphur in the process was explained by Liebig thus : potassium sulphate, which is always present in the potash, is reduced by carbon to sulphide, carbonate, and polysulphide. The latter dissolves iron, forming a double sulphide of iron and potassium which, when the product is lixiviated, dissolves in the potassium cyanide solution thus :

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$
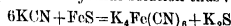
If insufficient iron is present in the fusion, the polysulphide is not entirely decomposed, and potassium sulphocyanide is also formed. R. Hoffmann (Annalen, 1860, 113, 81) investigated the behaviour of the sulphur compounds in the process in some detail, and found that the sulphur of potassium sulphide is rapidly and completely removed by iron alone in the fusion process, and that the same is true of potassium sulphate in presence of carbon. When organic matters are added to the sulphur-free melt, however, sulphocyanide is produced in proportion to the quantity added. Hoffmann, therefore, attributes its formation to the organic matter.

The behaviour of potassium sulphocyanide in the fusion is not clearly understood. Hoffmann found that it is completely decomposed by fusion with excess of potassium carbonate, yielding cyanate and sulphide ;[1] but if the mixture is again heated with carbon, the sulphocyanide is regenerated. It appears, therefore, that, under the conditions of the process, sulphocyanide is not decomposed. The reaction between iron and sulphocyanide is described below.

A part of the sulphide of iron formed is present in the form of a potassium ferrous sulphide, $FeS \cdot xK_2S$, which dissolves in hot water to a dark-green, colloidal solution which is coagulated by cooling or by adding excess of potassium carbonate. Another part is probably present in the form of the crystalline potassium ferric sulphide $K_4S \cdot Fe_2S_3$, obtained by K. Preis (J. pr. Chem. 1869, 107, 10), by fusing together finely divided iron, potassium carbonate, and sulphur. He found that the crystalline sulphide was formed at very high temperatures, and the amorphous one, yielding the green solution, at lower temperatures.

The reaction between potassium cyanide and ferric sulphide

$$13KCN + Fe_2S_3 = 2K_4Fe(CN)_6 + KSCN + 2K_2S$$
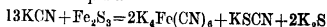
would give a ratio of cyanogen in the form of sulphocyanide to cyanogen in the form of ferrocyanide of 1 : 12, whilst Hoffmann, in 10 experiments, found ratios varying from 1 : 5 to 1 : 18.

The improvements in the process which were proposed aimed at saving the ammonia evolved in the early stages by distilling the organic matters separately and passing the ammonia

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[1] I can confirm the accuracy of this observation. Equal molecules of potassium carbonate and sulphocyanide were fused together in a closed aluminium crucible at 500°–580° for 1½ hours, a little more than half of the materials had reacted in accordance with the equation $KSCN + K_2CO_3 = KCNO + K_2S + CO_2$.—T. E.

through a red-hot mixture of potash and charcoal (Brunquell, Wagner's Jahresber. 1856, 2, 102), or a similar mixture with iron added (Karmrodt, *ibid.* 1857, 3, 139), or over red-hot charcoal forming hydrocyanic acid which was to be absorbed, together with the unchanged ammonia, in a solution of ferrous sulphate (Brunquell). These proposals, unfruitful at the time, are interesting as foreshadowing processes which came into successful operation nearly half a century later.

The belief, which prevailed until about the end of the nineteenth century, that cyanogen compounds are more easily produced from potash than from soda, is not entirely in accordance with the older experimental evidence. The truth appears to be that equally good results can be obtained with sodium carbonate under suitable conditions, but the conditions are not so easily realised.

L. Possoz (Compt. rend. 1858, 47, 209) obtained, under manufacturing conditions, 5 parts of sodium prussiate, instead of 25 parts of the potassium salt, from 100 parts of horn. R. Hoffmann (Annalen, 1860, 113, 81), using a very high temperature and sodium carbonate, got the equivalent of 11 parts of potassium ferrocyanide from 100 parts of woollen rags, against 10 to 14 parts with potash, and S. Tanatar (Dingl. poly. J. 1880, 237, 234) obtained the results tabulated below, as the means of 3 to 5 experiments :—

Blood charcoal	K₂CO₃	Na₂CO₃	NaCl	CaCO₃	Prussiate obtained
10	25	—	—	—	2·15
10	—	25	—	—	0·2
10	—	5	25	—	2 17
10	—	5	25	3	2·3

Manufacture of Potassium and Sodium Ferrocyanides.—(2) *From the products of distillation of coal.* The coal used in the manufacture of illuminating gas may be taken to contain from 1 to 1·9 p.c. of nitrogen (Drehschmidt, Journ. für Gasbeleuchtung, 1904, 677 ; J. McLeod, J. Soc. Chem. Ind. 1907, 26, 137). When the coal is distilled, a part of this nitrogen passes into the gas in the form of ammonia, hydrocyanic acid, and free nitrogen, a small part is found in the tar, and the remainder in the coke. The distribution of the nitrogen between these products varies considerably, being influenced by the nature of the coal, the amount of moisture in it, the temperature of distillation, and the kind of retort used. The following table indicates the magnitude of the quantities involved when the coal is distilled dry :

No.	Kind of coal	P.c. of the total N of the coal in				
		Coke	NH₃	HCN	Tar	Gas
1	Durham .	48·7	14·5	1·6	—	35·2
2	Westphalia	50	12–14	1·8	1·5	30·0
3		48	15	2	—	35
4	Scottish .	58·3	17·1	1·5	3·9	19·5

1. Foster, J. Gas Lighting, 1882, 1081.
2. Knublauch, J. Soc. Chem. Ind. 1896, 15, 106.

3. Chief Inspector of Alkali Works, 43rd Report, 1906, 58.
4. J. McLeod, J. Soc. Chem. Ind. 1907, 26, 137 ; and Alkali Works, 44th Report, 1907, 215.

The effect of temperature on the distribution of the nitrogen has been investigated by O. Simmersbach (J. Soc. Chem. Ind. 1915, 34, 895), using a Silesian coal containing 1·396 p.c. of N. The following table contains some of his results :

Temp.	P.c of the total nitrogen				
	as NH₃	as HCN	in tar	as N₂ in gas	in coke
600	7·81	0·25	2·12	18·13	71·69
800	21·28	0·87	3·47	10·73	63·65
1000	23·15	1·23	4·11	21·53	49·98
1200	22·84	1·42	4·21	· 45·10	26·43

Even the ammonia liquor from low temperature carbonisation retorts working at 427°–455°• contains traces of cyanogen compounds (Alkali Works, 45th Report, 1908, 52).

Hydrocyanic acid is converted into ammonia by water vapour at the temperature of distillation used in gas works and coke ovens

$$HCN + H_2O = NH_3 + CO$$
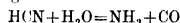
(Carpenter and Linder, J. Soc. Chem. Ind. 1905, 24, 63). The gas from coke ovens distilling coal with some 12 p c. of moisture therefore contains about two-thirds of the quantity of hydrocyanic acid found in the gas made from almost dry coal in gas works.

The gas leaving the retorts contains the whole of its cyanogen in the form of hydrocyanic acid (Alkali Works, 43rd Rep. 1906, 33), the fate of this depends on the process of purification adopted. In common practice about one-third of it is condensed along with the ammonia in the virgin liquor and ammonia scrubbers in English works (Alkali Works, 43rd Rep. 1906, 61), but less in many German works, where less water is used in the scrubbers (Bertelsmann, Technologie der Cyanverbindungon, 171). The greater part of this is converted into sulphocyanide, and escapes finally in the effluent from the ammonia stills. From 50 to 70 p.c. is caught in the iron oxide purifiers, the remainder passing away with the gas, where it is a source of damage to meters and gas-holders. A more complete recovery is obtainable when one of the cyanide washers described below is placed before the ammonia scrubbers. Up to 1908 attempts to recover cyanogen compounds from coke-oven gases had been unsuccessful (Alkali Works, 44th Rep. 1907, 40).

The total quantity of cyanogen compounds formed during the destructive distillation of coal is very considerable. In 1912 the world's production of ammonium sulphate was 1,144,000 tons. In Great Britain over 70 p.c. of the production came from gas works and coke ovens in which roughly one molecule of hydrocyanic acid accompanies ten molecules of ammonia. Assuming the same conditions in other countries, it appears probable that hydrocyanic acid equivalent to 80,000 tons of KCN is formed annually ; only a small part of this is actually recovered.

Formation of HCN from Ammonia and Carbon.

—The earliest synthesis of hydrocyanic acid was effected by Clouet (Ann. de Chim. 1791, 11, 30), by passing dry ammonia over wood charcoal heated to bright redness in a porcelain tube. This reaction has been studied quantitatively by E. Bergmann (Journ. für Gasbel. 1896, 39, 117), D. Lance (Compt. rend. 1897, 124, 819), G. A. Voerkelius (Dissertation, Hannover, 1909), and Carpenter and Linder (Alkali Works, 45th Rep. 1908, 26 ; 46th Rep. 1909, 21). The formation of hydrocyanic acid begins at about 700°, and the best yields, calculated on the ammonia used, are obtained at temperatures between 1000° and 1100°. The reaction $NH_3 + C \rightleftarrows HCN + H_2$ is reversible, and should lead to an equilibrium between ammonia, hydrocyanic acid, and hydrogen ; the equilibrium, however, cannot be realised, because both ammonia and hydrocyanic acid are unstable at the temperatures required. The final result depends, therefore, on the rates of decomposition of ammonia and hydrocyanic acid and on the rate of reaction between ammonia and charcoal. Even at 1000°, the rate of decomposition of hydrocyanic acid in presence of charcoal is small, but in presence of other substances it may be large. Voerkelius, for example, passed a mixture of hydrocyanic acid and hydrogen through an unglazed porcelain tube at 1000°, and found that over 70 p.c. of it was decomposed, but, after a layer of carbon had been deposited on the tube the decomposition fell to 19 p.c. The rate of decomposition of the ammonia is even more variable ; for example, at 720°, 28 p.c. of the ammonia survived 6 minutes' contact with fresh finely ground wood charcoal, whilst 82 p.c. were unchanged when the charcoal was in the form of lumps which had been already used. The rate of decomposition of the ammonia is diminished by diluting it with an indifferent gas.

In the 66 experiments recorded by Voerkelius, the ammonia (diluted with hydrogen) was in contact with the charcoal for from 16 to 360 seconds ; within these limits, the ratio between the numbers of molecules of ammonia and of hydrocyanic acid in the product is roughly independent of the time of reaction, but the quantity of ammonia decomposed into its elements increases with the time of contact. The following table is calculated from the figures given by Voerkelius. The figures show the influence of the quality of the charcoal on the result :—

Temperature		P.c. NH₃ in gas used	Mols. HCN in product
			Mols. NH₃
720° charcoal A		50	6·7–13·4 mean 9·80
,, B		50	29–45 ,, 37·7
sugar charcoal		50	71 ,, 71
1020° charcoal C		13–15	0·64–0·92 ,, 0·76
,, D		13–15	0·90–1·80 ,, 1·40
,, C		43–47	0·50–0·90 ,, 0·61
1120° ,, D		13·4	0·44–0·48 ,, 0·46

Nernst's thermodynamic theorem (Application of Thermodynamics to Chemistry, London) 1907, and Theoretische Chemie, 5th and 6th ed. has been applied to this reaction by v. Wartenberg (Zeitsch. anorg. Chem. 1907, 52, 299). Since the reaction $NH_3 + C = HCN + H_2$ absorbs 39,500 cals. per molecule, the equilibrium must

lead to the formation of more hydrocyanic acid at higher temperatures, the calculation indicates that the ratio of the partial pressures (in atmospheres) of the gases in equilibrium should have the following values :—

Temperature	$\dfrac{p_{NH_3}}{p_{HCN} \times p_{H_2}}$
500°	632
800°	0·27
1100°	0·003
1400°	0·0002

In the experiments tabulated above, the final mixture of gases usually contained nearly 95 p.c. of hydrogen, the partial pressure of which was therefore almost 1 atmosphere. The molecular ratio of ammonia to hydrocyanic acid is, therefore, almost the same as the ratio of the partial pressures. A comparison of the experimental values with those calculated shows that equilibrium is never even approximately attained. They agree in indicating 700° as the lowest temperature at which appreciable quantities of hydrocyanic acid can be formed.

Carpenter and Linder's independent investigation yielded results in close agreement with those obtained by Voerkelius. It seems fairly certain that the greater part of the hydrocyanic acid found in the products of destructive distillation of coal is formed by the reaction which has just been discussed. The presence of small quantities of HCN in the products formed at temperatures below 600° indicates, however, that it may be, in part, a primary product of the decomposition.

Spent oxide. The hydrated oxide of iron first used in gas purification was made by mixing ferrous sulphate and slaked lime, sawdust being added to increase the porosity (Laming, Eng. Pat. 11944, of 1847); natural iron ores were introduced by Howitz in 1870. Sulphuretted hydrogen is absorbed, yielding a mixture of ferrous and ferric sulphides which is regenerated by exposure to air and moisture, free sulphur and ferrous and ferric hydroxide being produced. Ferrocyanide is formed from the ferrous hydroxide and ammonium cyanide, and then converted into Prussian blue by interaction with the ferric iron. Sulphocyanides are also formed in very variable amount, doubtless by the interaction of hydrocyanic acid and ammonium polysulphide. Since ammonia, sulphuretted hydrogen, and free sulphur are always present in the purifiers, it is obvious that polysulphides of ammonium can always be formed ; it appears to be generally allowed, however, that sulphocyanide is only produced in large amount when the mixture becomes warm, as, for example, when the regeneration proceeds rapidly in a large mass of material. The spent oxide finally contains 30 to 40 p.c. of sulphur (or more), soluble ammonium salts and Prussian blue, in addition to tar and iron oxides. Good material contains 11 to 12 p.c. of Prussian blue, calculated on the air-dried substance, whilst ammonium sulphocyanide varies from traces to 10 p.c.

As already mentioned, prussiates were first produced from spent oxide by Gautier-Bouchard about 1860. Ammonium salts were first removed by washing with water ; the residue was then mixed intimately with sufficient lime to

convert the Prussian blue into calcium ferro-cyanide and the mixture submitted to systematic lixiviation with cold water. This operation must be done in the cold, because otherwise calcium polysulphide is produced from the lime and free sulphur, and this converts the ferro-cyanide into sulphocyanide. The calcium ferro-cyanide was converted into the potassium salt by means of potassium carbonate, and the sulphur in the extracted residue burned to sulphur dioxide and converted into sulphuric acid (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63). This process contains the essential features of all those which have since been worked successfully.

T. L. G. Bell (Eng. Pat. 257, of 1868) proposed to extract the sulphur with carbon disulphide, and, after removing soluble ammonium salts with water, to boil the residue with lime. In order to obtain a pure product, the solution was then acidified and precipitated by the addition of ferric chloride, the Prussian blue being then converted into potassium ferro-cyanide. The preliminary extraction of the sulphur has occasionally been carried out, but it is difficult to separate the sulphur from the tar which is extracted along with it. In spite of the great difficulty of filtering and washing Prussian blue, this method of purification appears to have been fairly generally used up to the year 1883, when Kunheim and Zimmermann (Eng. Pat. 3342, of 1883) described two new methods.

In the first, the ammonia is only partially removed from the spent oxide by the preliminary washing, enough being left behind to produce the double salt $Ca(NH_4)_2Fe(CN)_6$. The extraction with lime then yields an ammoniacal solution of calcium ferrocyanide, which, when neutralised with hydrochloric acid and heated to 80°, deposits the very sparingly soluble calcium ammonium ferrocyanide, which is comparatively easily filtered and washed.

By the second method, the solution of calcium ferrocyanide, obtained by following Gautier-Bouchard's original procedure, is treated with a solution of potassium chloride which precipitates the double salt $CaK_2Fe(CN)_6$ in minute crystals, which are very readily washed and are then converted into potassium ferro-cyanide by boiling with potassium carbonate. By this means one-half of the potassium carbonate is replaced by the cheaper chloride, and a very pure product is obtained (Franz Bössner, Die Verwerthung der Ausgebrauchten Gasreinigungsmassen, 1902). From the calcium ammonium salt, sodium ferrocyanide is readily obtained.

During the decade 1885 to 1895, the spent oxide of the gas works was the principal source of prussiates; its importance, however, has been diminished by the introduction of the more efficient wet methods of recovering the hydrocyanic acid.

Cyanide Washers.—The first practicable proposal of this kind was made by O. Knublauch (Eng. Pat. 15164, of 1887). Coal gas was to be scrubbed with a solution of the oxide, hydroxide, carbonate, or sulphide of ammonium, or of an alkali or alkaline-earth metal containing the hydroxide or carbonate of iron, zinc, or manganese in suspension. The process did not succeed

at the time, probably for commercial reasons. The very similar process of Foulis (Eng. Pat. 9474, of 1892; Foulis and Holmes, Eng. Pat. 15168, of 1895) has since been introduced at several gas works with satisfactory results. In this process, the reagent required is prepared by precipitating a ferrous salt with sodium carbonate. The washed precipitate (a partially oxidised mixture of ferrous carbonate and hydroxide) is suspended in a solution of sodium carbonate and the gas passed through it in a rotary scrubber. Foulis wished to obtain the whole of the ferrocyanide in the form of a solution of the sodium salt, and therefore placed the cyanogen washer after the ammonia scrubbers because, in presence of ammonia, an insoluble ammonium ferrous ferrocyanide is formed which is only decomposed by sodium hydroxide, but not by the carbonate. At the Hague gas works, however, this order was reversed in order to catch the hydrocyanic acid which is otherwise condensed along with the ammonia (Rutten, Journ. of Gas Lighting, 1902, 80, 879; Jorrisen and Rutten, Journ. für Gasbeleuchtung, 1903, 716). The saturated liquor from the cyanide washer contains Prussian blue and potassium and ammonium ferrous ferrocyanides in suspension and potassium ferrocyanide and ammonia in solution (potassium carbonate is used instead of the sodium salt). This mixture is filter-pressed and the solution distilled to separate the ammonia and then evaporated *in vacuó* and crystallised. The press cake is boiled with caustic potash and the ammonia collected, the residual iron oxide returning to the cyanide washer, and the solution of ferro-cyanide going to the evaporating plant.

In another set of proposals, the use of an alkali other than the ammonia of the gas is dispensed with, the crude coal gas being simply washed with a solution of ferrous sulphate. Since ammonia and sulphuretted hydrogen are present in much larger quantities than hydrocyanic acid, the ferrous sulphate is soon converted into a suspension of ferrous sulphide in a solution of ammonium sulphate, and the subsequent changes may be regarded as due to the action of a solution of ammonium cyanide on ferrous sulphide. If a large excess of the latter is present, the main product is ferrous ferro-cyanide $Fe_2[Fe(CN)_6]$; as the ferrous sulphide is used up, ammonium ferrous ferrocyanide $(NH_4)_2Fe[Fe(CN)_6]$ is formed in increasing quantities, and finally, when but little FeS remains, ammonium ferrocyanide is found in solution (Feld, Journ. für Gasbeleuchtung, 1904, 132).

The earlier patentees of processes based on these reactions attempted to obtain the ferro-cyanide in a soluble form by using a dilute solution of a ferrous salt, and so having a large excess of ammonia present (Rowland, Eng. Pat. 22347, of 1891; Lewis and Cripps, Eng. Pat. 20883, of 1896; Schröder, Eng. Pat. 19849, of 1898; Teichmann, Eng. Pat. 12485, of 1899), but since insoluble compounds are always formed to some extent, it appears to be easier to obtain all the ferrocyanide (or the greater part of it) in the insoluble form by using a saturated solution of ferrous sulphate, and so having a large excess of iron present as first proposed by Bueb (Eng. Pat. 9075, of 1898). Bueb's process

has been adopted by a considerable number of gas works. It is said to absorb 98 p.c. of the hydrocyanic acid in the gas, yielding a mud containing 6-7 p.c. of ammonia and cyanogen compounds, equivalent to 18-20 p.c. of yellow prussiate of potash. A small part of the ferrocyanide is in solution. This is precipitated by boiling the mixture with ferrous sulphate; the precipitate is then filtered off and treated with lime, the calcium ferrocyanide solution obtained being worked up in the way already described when dealing with spent oxide.

As already mentioned, part of the hydrocyanic acid in coal gas is always converted into sulphocyanide owing to liberation of free sulphur by the action of atmospheric oxygen on sulphuretted hydrogen. By suitable means the whole of the hydrocyanic acid may be fixed in the form of sulphocyanide, which is then converted into ferrocyanide by one of the processes described in the next section.

In 1877 W. Marriott (Eng. Pat. 3311, of 1877) proposed to scrub gas with a solution of sodium polysulphides, and in 1888 Campbell and Boyd (Eng. Pat. 10186, of 1888) proposed the use of manganese dioxide suspended in water. This liberates sulphur from a part of the sulphuretted hydrogen in the gas, and this free sulphur combines with ammonium sulphide to form polysulphide, which converts the cyanide into sulphocyanide. The final step, which led to a successful and economical process, was made by H. Wood Smith (H. Wood Smith, Gidden, Salamon, and Albright, Eng. Pat. 13658, of 1901) by simply scrubbing the gas through a suspension of sulphur, whereby the hydrocyanic acid is removed quantitatively, and a solution containing as much as 200 grams of ammonium sulphocyanate per litre may be obtained. This process is in use at several gas works, and yields practically the whole of the sulphocyanides made at present.

Manufacture of Sodium and Potassium Ferrocyanides.—(3) *From Sulphocyanides.* A. Gélis (Eng. Pat. 1816, of 1860) was the first to manufacture potassium ferrocyanide by heating dry potassium sulphocyanide with iron, made by reducing the oxide, at a dull-red heat, in a closed vessel. He states that too high a temperature leads to considerable loss. The fusion process yields a mixture of potassium cyanide and ferrous sulphide which gives potassium ferrocyanide, when treated with water in the same way as the 'metal' of the old process (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63). Sir G. Beilby has informed the writer that he made considerable quantities of potassium ferrocyanide by this process in the years 1873–1876. Potassium sulphocyanide was heated with iron turnings in air-tight iron retorts and, after cooling sufficiently, the product was extracted with water in the retort itself, without coming in contact with air. In this way the only serious difficulty of the process, which is due to the extreme proneness to oxidation of the fusion product, is avoided and satisfactory yields obtained.

The process was taken up again in 1878 by Günzburg and Tcherniac (Eng. Pat. 1148, of 1878; 1359, of 1879; 1261, of 1881). They dried the sulphocyanide by fusing it at 300°, and then mixed it intimately with the oxide-free

iron by grinding them together. The mixture was heated in iron boxes with closely fitting covers at 445°, the vapour of boiling sulphur being used to obtain a constant temperature. After working for two or three years, the process was given up, but it was revived for the third time in 1894 by the United Alkali Co., Ltd. (Hetherington and Muspratt, Eng. Pat. 5830, of 1894), and by the British Cyanides Co., Ltd. (Crowther, Rossiter, Hood and Albright, Eng. Pat. 8305, of 1894). The patent specifications of Hetherington and of Crowther add but little to the information given above. In both cases, some 20 to 30 p.c. excess of iron is used, and the temperature is almost the same as that recommended by Günzburg and Tcherniac. Crowther says that mere fusion is insufficient to dry the sulphocyanide; a current of an indifferent gas must be passed through it for some time. Conroy (J. Soc. Chem. Ind. 1896, 15, 12) was able, in a small scale experiment, to convert 76·8 p.c. of the sulphocyanide used into ferrocyanide (leaving 18·2 p.c. unchanged) by means of Hetherington's method. The process has been worked by the British Cyanides Co. at Oldbury since 1894 (Brussels Exhib. 1910, Catalogue of British Chem. Section, 155).

The conversion of sulphocyanides into ferrocyanides is also possible in aqueous solution. Sternberg (D. R. P. 32892, of 1882), found that by heating a solution of potassium sulphocyanide with double the theoretical quantities of iron filings and ferrous hydroxide under pressure at 110°-120°, about 80 p.c. of the material could be converted into ferrocyanide in accordance with the equation

$$6KCNS + 6Fe + Fe(OH)_2 = 6FeS + K_4Fe(CN)_6 + 2KOH$$
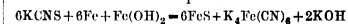
G. R. Bower (Eng. Pat. 361, of 1896) succeeded in removing the sulphur from ferrous sulphocyanide by means of copper in a similar way: $Fe(CNS)_2 + 2Cu = 2CuS + Fe(CN)_2$. Conroy (Conroy, Hurter, and Brock, Eng. Pat. 3867, of 1896; J. T. Conroy, J. Soc. Chem. Ind. 1898, 17, 98) then found that a mixture of a soluble sulphocyanide and a ferric or ferrous salt would do as well as pure ferrous sulphocyanide, and also that the sulphur is more rapidly removed by finely divided iron than it is by copper. Using very finely divided iron, the reaction takes place quantitatively in 5 to 6 hours at a temperature of 135°-140° and a pressure of 50 to 60 lbs. per square inch, in accordance with the empirical equation $Fe(CNS)_2 + 2Fe = Fe(CN)_2 + 2FeS$. (Sodium or potassium sulphocyanide is acted on by iron under similar conditions very slowly and incompletely.) The black mud produced is either boiled with caustic alkali to decompose the ferrous ferrocyanide, or the ferrous sulphide is first dissolved in hydrochloric acid. The latter course is to be preferred, owing to the fact that ferrous sulphide combines with the alkalis, each 3 or 4 equivalents of it rendering 1 equivalent of either caustic soda or potash insoluble, a difficulty with which the manufacturers of ferrocyanide from nitrogenous organic matter had long been familiar.

PROPERTIES OF THE FERROCYANIDES.

The principal characteristics of those salts which possess some technical interest are described here; further information is to be

found in Cyanogen Compounds, by H. E. Williams, 1915, or in the text-books of inorganic chemistry.

Ammonium ferrocyanide is readily prepared in aqueous solution from the free acid and ammonia, or from barium ferrocyanide and ammonium sulphate. The solid salt

$$(NH_4)_4Fe(CN)_6,3H_2O$$
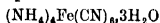
is obtained by evaporating the solution *in vacuô*, or by precipitation with alcohol. The salt crystallises with difficulty in very pale yellow plates, which are isomorphous with potassium ferrocyanide (Bunsen, Pogg. Ann. 1835, 36, 404). The aqueous solution decomposes when boiled, yielding ammonium cyanide and an insoluble residue, which possibly consists of more or less oxidised ammonium ferrous ferrocyanide

$$2(NH_4)_4Fe(CN)_6 = (NH_4)_2Fe[Fe(CN)_6] + 6NH_4CN$$
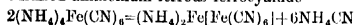
From solutions containing much ammonium chloride a double salt of the formula

$$(NH_4)_4Fe(CN)_6 \cdot 2NH_4Cl + 3H_2O$$
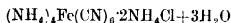
crystallises very readily in well-formed orange-yellow rhombohedra, which were at one time mistaken for the ammonium salt (Bunsen, *l.c.*).

Barium ferrocyanide $Ba_2Fe(CN)_6,6H_2O$ is precipitated when strong solutions of barium chloride and sodium ferrocyanide are mixed; it separates in the form of a light yellow, crystalline powder. Its solubility (grams of anhydrous salt per 100 grams water) is 0·34 at 15·5°, and 1·01 at 100° (Williams). The water of crystallisation is not quite completely driven off even at 160° (Drechsel, J. pr. Chem. 1880, [2] 21, 77). The dried salt, when heated *in vacuô*, or in an atmosphere of nitrogen, begins to decompose at about 500°, nitrogen, carbon, iron, and barium cyanide and cyanamide being formed. When oxygen is completely excluded the product contains about 2 molecules of cyanamide to 1 of cyanide (Ewan and Napier, J. Soc. Chem. Ind. 1913, 32, 467).

Barium potassium ferrocyanide

$$BaK_2[Fe(CN)_6],3H_2O$$
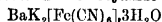
is precipitated as a pale yellow, crystalline powder when solutions of barium chloride and potassium ferrocyanide are mixed in equivalent quantities. Its solubility in water (grams anhydrous salt per 100 grams water) is 2·1 at 15·5°; 6·08 at 100°.

Calcium ferrocyanide $Ca_2Fe(CN)_6,12H_2O$ is extremely soluble in water; highly concentrated solutions are very viscous and crystallise with difficulty, yielding small yellow triclinic crystals of sp.gr. 1·68, which effloresce when exposed to the air and lose 11½ molecules of water at 40°. H. G. Colman (Journ. of Gas Lighting, 1910, 583) finds that the whole of the water is removed by heating the salt in a current of air. The dry salt begins to decompose (in absence of oxygen) at 500° yielding calcium cyanamide thus

$$Ca_2Fe(CN)_6 = 2CaCN_2 + Fe + N_2 + 4C$$
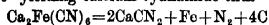
(unpublished experiments made by the writer).

Calcium ammonium ferrocyanide

$$Ca(NH_4)_2Fe(CN)_6$$
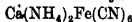
is a white, minutely crystalline powder, which becomes coloured on exposure to light; it is anhydrous; 100 grams of water, at 15°–17°, dissolve 0·258 gram of the salt (J. Campbell Brown, Chem. Soc. Trans. 1907, 91, 1826)

Calcium potassium ferrocyanide $K_2CaFe(CN)_6$ is a white powder consisting of small quadratic prisms which becomes slightly cream-coloured on exposure to light. It contains no water of crystallisation and, at 15°–17°, 100 grams of water dissolve 0·41 gram of it (J. Campbell Brown, *ibid.* 1907, 91, 1826).

According to Williams (*l.c.*), the solubilities of these salts are rather larger, viz. 0·35 at 15°, and 0·39 at 100° for the ammonium salt; and 0·72 at 15°, and 0·80 at 100°, for the potassium salt.

Cupric ferrocyanide $Cu_2Fe(CN)_6 \cdot 11H_2O$ is a red-brown, amorphous substance, obtained by adding a solution of calcium ferrocyanide or hydroferrocyanic acid to excess of cupric chloride solution. In general, when solutions of a cupric salt and of a soluble ferrocyanide are mixed, an insoluble substance is produced, in which only a part of the four valencies of the ferrocyanogen ion is saturated by copper, the remainder being occupied by the metal of the ferrocyanide employed. A very large number of these substances have been described. Colloidal membranes formed of one or other of these copper ferrocyanides have been much used in the study of osmosis. The precipitate formed from potassium ferrocyanide and a cupric salt $K_6Cu_4[Fe(CN)_6]_3$ was used as a pigment under the name Hatchett's brown. The black, silver deposit in an ordinary photographic 'bromide' print may be converted into a red one, consisting of a copper ferrocyanide, by immersing the print in a solution containing 6·6 grams of copper sulphate crystals, 88 grams of potassium citrate, and 5·8 grams of potassium ferricyanide per litre (Ferguson, Photographic Journ. 1900, 133).

Cuprous ferrocyanide $Cu_4Fe(CN)_6 \cdot xH_2O$ is a white precipitate, which differs from most of the ferrocyanides in evolving the whole of its cyanogen as hydrocyanic acid when boiled with dilute sulphuric acid. J. Dewrance and H. E. Williams (Eng. Pat. 28074, 1908) utilise this property in order to obtain complete decomposition of alkali ferrocyanides by distilling them with acid in presence of a small amount of cuprous chloride.

Hydroferrocyanic acid $H_4Fe(CN)_6$ is prepared by adding concentrated hydrochloric acid to a saturated solution of potassium ferrocyanide (both should be free from dissolved oxygen) and then enough ether to saturate the solution. The acid crystallises out in colourless scales which are washed with water saturated with ether (A. W. Williamson, Annalen, 1846, 57, 225; A. Joannis, Ann. Chim. Phys. 1882, [5] 26, 484), and dried over sulphuric acid. It may be purified by dissolving in alcohol and precipitating with ether; it obstinately retains ether, which is removed by heating at 100° in a current of dry hydrogen (Browning, Chem. Soc. Trans. 1900, 1234). A solution of the acid, saturated at 14°, contains 150 grams per litre. The solution is readily oxidised by atmospheric oxygen, especially at higher temperatures, forming a blue substance which is usually assumed to be Prussian blue. This reaction is utilised in calico printing for the production of blue patterns.

Ferrous ammonium ferrocyanide

$$Fe(NH_4)_2Fe(CN)_6]$$
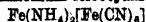
is formed when a solution containing ammonium ferrocyanide and excess of an ammonium salt is exactly precipitated by a ferrous salt, oxygen being excluded. It is also formed when ammonium ferrocyanide is distilled with an acid in absence of air.

Ferrous cyanide $Fe(CN)_2$ is formed when a solution of hydroferrocyanic acid is boiled, $H_4Fe(CN)_6 = 4HCN + Fe(CN)_2$, or when the dry acid is heated at 300° in an atmosphere of hydrogen (Addie and Browning, Chem. Soc. Trans. 1900, 158; Browning, *ibid.* 1900, 1234).

Ferrous potassium ferrocyanide (Everitt's salt) $K_2Fe[Fe(CN)_6]$ is formed in a similar way if potassium salts are present, as, for example, in the preparation of hydrocyanic acid by distilling a mixture of potassium ferrocyanide and dilute sulphuric acid. Everitt's salt is a pale-yellow crystalline powder which is not identical with the white precipitate obtained by mixing solutions of potassium ferrocyanide and ferrous chloride, although this precipitate has the same composition.

The iron in these ferrous salts is displaced by treatment with caustic alkalis, but not by alkali carbonates.

Ferric ferrocyanides. The blue compounds of iron and cyanogen are all amorphous substances, which yield colloidal solutions in pure water. It is therefore extremely difficult to prepare them in a pure condition. Owing to the well-known tendency of colloids to adsorb other substances from solutions, the precipitates require very prolonged washing to free them from adhering salts, and during this process their composition may, and very often does, change, owing to atmospheric oxidation or to hydrolysis. On the other hand, the method of determining the composition of a precipitate by mixing known quantities of the reagents and estimating the excess left in the supernatant liquid, is open, in this case, to the objection that the precipitate is not a pure substance because it has adsorbed some of the salts in the solution in contact with it. This method has been used by E. Müller and by P. Woringer. (E. Müller and T. Stanisch, J. pr. Chem. 1909, [ii] 79, 81; *ibid* 1909, [ii] 80, 153; E. Müller, G. Wegelin, F. R. Treadwell, and O. Diefenthaler, *ibid.* 1911, [ii] 84, 353; E. Müller, *ibid.* 1914, [ii] 90, 119; P. Woringer, ibid. 1914, [ii] 87, 51.) K. A. Hofmann and his collaborators (K. A. Hofmann, O. Heine, and F. Höchtlen, Annalen, 1904, 337, 1; K. A. Hofmann and F. Resensheck, *ibid.* 1905, 340, 267; 1905, 342, 364; Hofmann, Arnoldi, and Hiendlmaier, *ibid.* 1907, 352, 54), have investigated more especially the composition and properties of the substances which remain after exhaustive purification.

The freshly prepared blue precipitates contain indefinite quantities of water, but the whole of it cannot be removed by drying *in vacuo* over phosphorus pentoxide until a constant weight is attained (which usually requires from 2 to 5 months). This residual water must be regarded as constitutional, because when the precipitates are heated to temperatures a little above 100°, they lose hydrocyanic acid, but not water. The formulæ of the dry substances given in what follows refer to the very thoroughly washed substances after complete drying over P_2O_5 in the way mentioned above.

When cold neutral solutions of one molecule of a ferric salt and one molecule of potassium ferrocyanide are mixed together, a precipitate of ordinary soluble Prussian blue is formed. The dry substance has the composition

$$2[KFe^{III}(Fe^{II}Cy_6)] + 3\tfrac{1}{2}H_2O$$
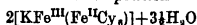
The same compound is obtained by mixing equal molecular quantities of a ferrous salt and potassium ferricyanide. This was first proved by Skraup (Annalen, 186, 371, 1877).

When a cold solution of potassium ferrocyanide is added gradually to a cold neutral (or $\tfrac{1}{2}$ p.c. hydrochloric acid) solution containing an excess of a ferric or of a ferrous salt, or when soluble Prussian blue is digested with a solution of ferric chloride, precipitates are formed which, after the prolonged exposure to air involved in washing them completely, are identical in composition and properties. The dry substance is normal ferric ferrocyanide

$$Fe_4^{III}(Fe^{II}Cy_6)_3 + 10H_2O$$
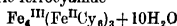
usually referred to as Prussian blue. Turnbull's blue, obtained by precipitating a solution of potassium ferricyanide with an excess of a ferrous salt, is, after exhaustive washing and exposure to air, identical with ordinary Prussian blue.

The composition of the unwashed precipitates initially formed depends, as Müller has shown, on the relative quantities of reagents employed. Setting out from potassium ferrocyanide and ferric chloride, Prussian blue is precipitated when the ratio mols. $K_4Fe(Cy_6)$/mols. $FeCl_3$ is less than 0·75; for values between 0·75 and 0·92 the precipitate contains increasing quantities of $KFe^{III}[Fe^{II}Cy_6]$, and when the ratio exceeds 0·92 the substance
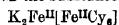
$$K_2Fe^{II}[Fe^{II}Cy_6]$$

is also present. Setting out from potassium ferricyanide and ferrous chloride a precipitate of the composition $KFe^{II}Fe_5^{III}[Fe^{II}Cy_6]_5$ is obtained when the ratio, mols. K_3FeCy_6/mols. $FeCl_2$ is less than 0·714. Between 0·714 and 0·75 a substance $KFe^{II}Fe_3^{III}[Fe^{II}Cy_6]_3$ is formed, which Müller regards as ordinary Turnbull's blue; from 0·75 to 0·9 increasing quantities of $KFe^{III}[Fe^{II}Cy_6]$ are present, and finally, when the ratio exceeds 0·9 ordinary Prussian blue appears. According to Müller, Turnbull's blue and Prussian blue are interconvertible

$$Fe_4^{III}[Fe^{II}Cy_6]_3 + K^{\cdot} + Fe^{\cdot\cdot}$$
$$\rightleftarrows KFe^{II}Fe_3^{III}[Fe^{II}Cy_6]_3 + Fe^{\cdot\cdot\cdot},$$
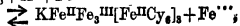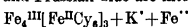
although a very large excess of ferrous salt is required to convert an appreciable amount of Prussian blue.

It is obvious that the reactions involved in the formation of the blues are not simple double decompositions; mutual oxidations and reductions take place, and adsorption phenomena are superadded, so that, in general, the precipitates first produced are mixtures either of definite insoluble compounds, as Müller supposes, or if insoluble substances with soluble constituents adsorbed from the solutions.

The precipitates obtained from hot acid solutions differ more or less from those formed at ordinary temperatures in their properties, and appear even when washed to be mixtures of different substances.

Both the soluble and insoluble Prussian blue, above described, are ferric ferrocyanides, and not ferrous ferricyanides. This is proved by the fact that they can be made by the action of hydrogen peroxide on a solution containing a ferric salt and potassium ferricyanide in suitable quantities. As Schönbein (J. pr. Chem. 1866, 98, 65) showed, hydrogen peroxide reduces ferricyanide to ferrocyanide, but has no action on a ferric salt, so that ferrous ferricyanide could not be produced by this reaction.

Blue compounds, which are not identical with those described above, are also obtained by the oxidation of ferrous ferrocyanides.

(a) By adding a cold neutral solution of 1 molecule of a ferrous salt to a solution of 1 molecule of potassium ferrocyanide, and then oxidising the white precipitate by means of atmospheric oxygen, which is greedily absorbed (or better by hydrogen peroxide), a blue compound of the composition $KFe^{III}(Fe^{II}Cy_6)+H_2O$ is obtained. This differs from ordinary soluble blue in being insoluble in oxalic acid solution. It is referred to in the table of properties of the blues as K. A. Hofmann's blue.

(b) By proceeding exactly as in (a), except that the solutions contain 1 p.c. of sulphuric acid, a white precipitate is obtained, $Fe^{II}K_2(Fe^{II}Cy_6)$, which is rather less readily oxidised to a blue of the same composition as before :

$$Fe^{III}K(Fe^{II}Cy_6)+H_2O$$

but possessing rather different properties. Like ordinary soluble Prussian blue, it is soluble in water and oxalic acid, but differs from it in being much more stable to ammonia solution. This compound is referred to as 'stable soluble blue.'

(c) When a solution of potassium ferrocyanide, containing about 10 p.c. of sulphuric acid, is heated in an atmosphere devoid of oxygen, one half of the hydrocyanic acid is evolved and a pale-yellow crystalline powder of Everitt's salt $K_2Fe^{II}Cy_6)$ remains behind. This salt is very much less readily oxidised than the precipitate obtained by mixing solutions of potassium ferrocyanide and a ferrous salt ; it is not completely oxidised by several weeks' exposure to the air. It is readily oxidised by warm dilute nitric acid (A. W. Williamson, Ann. Chem. Pharm. 1846, 57, 225), but a homogeneous product is prepared most certainly by suspending it in 1 p.c. sulphuric acid and adding about 10 times the theoretical quantity of hydrogen peroxide. The substance thus obtained is Williamson's blue (sometimes called violet), and it also has the composition

$$KFe^{III}(Fe\ Cy_6)+H_2O$$
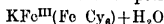
Its properties are, however, totally different from those of the isomeric substances already described.

PROPERTIES OF THE BLUE IRON-CYANOGEN COMPOUNDS.

Reagent	Ordinary soluble Prussian blue (Turnbull's soluble blue).	Insoluble Prussian blue	K. A. Hofmann's blue	Stable soluble blue	Williamson's blue or violet
Pure water .	Soluble, reddish-blue solution	Insoluble	Soluble, greenish-blue solution	Soluble	Insoluble, turbid greenish-blue suspension
10 p.c. oxalic acid	Soluble, blue solution	Soluble, blue solution	Insoluble	Soluble	Insoluble
4 p.c. ammonia	yields red-brown ferric hydroxide	In a few seconds	In 10 seconds	In a few seconds	In 6 to 7 minutes	After some hours
Ferric chloride	Precipitates insoluble Prussian blue	No change	(?)	Gradually coagulated in unchanged condition	No change
1 to 1½ p.c. H_2SO_4	Slowly precipitated ; moist precipitate soluble in water	No action	Quickly precipitated ; insoluble in water	Precipitated, insoluble in water	No action
Appearance of dry solids	Deep-blue with coppery lustre	Deep-blue purple lustre	—	—	Purple-red

For comparison, the distinguishing properties of the different blues are tabulated above. The isomerism of these substances may be due to differences in the linking of the atoms—of the kind familiar in organic chemistry—or it may be due to differences in the size of the molecules ; the data available do not appear to be sufficient to decide these questions with any degree of certainty.

In accordance with the commonly accepted view, the blues have been formulated as ferro-

cyanides. P. Woringer, in 1914 (l.c.), however, advanced certain arguments in favour of the ferricyanide structure. He confirmed an observation, made by A. W. Williamson in 1846, that when ferric chloride acts on an excess of ferrocyanide the solution contains ferricyanide ; he also states that Prussian blue, when decomposed by ammonium carbonate, yields 90 p.c. of ferricyanide. As E. Müller pointed out in 1909, it is easy to show, from the well-known oxidation potentials of solutions of ferrous

and ferric ions and of ferro- and ferri-cyanogen ions that, if these four ions could coexist in solution the ratio of their concentrations $[Fe]\cdot\cdot[FeCy_6]\cdot\cdot\cdot]/[Fe][Fe\cdot\cdot\cdot Cy_6\cdot\cdot\cdot\cdot]$ would be about 10^6, that is, ferrocyanide would be oxidised practically completely by ferric salts.

Williamson, however, showed that the reverse reaction also takes place, ferricyanide being partly reduced by ferrous salts. It appears thus that ferri- and ferro-cyanogen ions can coexist in approximately equal concentration, so that, in equilibrium, the concentration of ferric ion must be very small compared with that of ferrous ion. These concentrations are determined by the solubilities of the precipitates formed, about which very little appears to be known; the mode of formation of a blue affords, therefore, no certain clue to its structure. The same is true of its decomposition by strong alkalis, since alkaline ferricyanide solution oxidises ferrous hydroxide very readily. Hofmann's methods of preparation by means of hydrogen peroxide appear at present to be the best evidence available in favour of the ferrocyanide structure.

It is of interest that precipitation from hot acid solutions always tends to produce substances (or mixtures) of a more stable type, approaching Williamson's blue more or less closely in properties, and also that all the blue iron cyanogen compounds contain both ferrous and ferric iron. The compounds which contain only ferrous or only ferric iron are colourless or (compared with the blues) feebly coloured. Solid pieces of ordinary Prussian blue assume a coppery lustre when rubbed on a smooth, hard surface. The blue solution in oxalic acid was formerly used as an ink. Prussian blue is reduced by hydrosulphurous acid, $H_2S_2O_4$, or its sodium salt to white ferrous ferrocyanide (M. Rohn, Zeit. Anorg. Chem. 1906, 49, 443). Chlorine turns a suspension of Prussian blue in water green; the solution contains ferric chloride; the blue colour is restored by washing with water. Concentrated sulphuric acid unites with Prussian blue to a white paste from which the original blue is obtained by diluting with water. It is slowly decomposed by concentrated aqueous hydrochloric acid, but dissolves to a colourless solution in alcoholic hydrochloric acid; the solubility increases with the molecular weight of the alcohol used. Water precipitates unchanged Prussian blue from these solutions. By dissolving impure Prussian blue in a solution of hydrochloric acid in propyl alcohol, filtering, and reprecipitating with water, it may be separated from all commonly occurring impurities, such as barium sulphate, kaolin, alumina, and starch (C. Coffignier, Bull. Soc. chim. 1904, 391). Potassium, sodium, and calcium hydroxides decompose Prussian blue into ferric hydroxide and a ferrocyanide; alkali carbonates act more slowly. Tissues dyed with Prussian blue gradually lose their colour in sunlight, but regain it in the dark. When heated to 170° in the air, it burns like tinder leaving a brown ash.

Colloidal solutions of Prussian blue (0·2 to 2 p.c.) may be prepared by dialysis of the oxalic acid solution. The colloidal blue is negatively charged and is coagulated by cathions; hydrogen is especially active, otherwise the usual increase of activity with valency obtains (W. Pappadà, Gazz. chim. Ital. 1911, 41, ii. 454). K. A. Hofmann (Annalen, 1905, 340, 267) also observed that his soluble blue carried a negative charge, and did not depress the freezing-point.

Commercial blues are usually mixtures of the compounds already described. J. G. Gentele (Lehrbuch der Farbenfabrikation, 2nd ed. 1880) says that the best blues are obtained by precipitating a ferrous salt with potassium ferrocyanide, and then oxidising the precipitate. *Paris blue* (the finest quality of commercial Prussian blue) is made as follows : 50 kilos. of potassium ferrocyanide are dissolved in 250 kilos of boiling water ; 42·5 to 45 kilos. of green vitriol are dissolved in about the same quantity of water, preferably in the presence of scrap iron to prevent formation of ferric salt. The clear solutions are then run simultaneously into 250 kilos. of water. The almost white precipitate is allowed to settle and then drained on a cloth filter. The oldest method of ' blueing ' the paste was to heat it to boiling in a basin, transfer it to a wooden tub, and add 25·5 kilos. of nitric acid (sp.gr. 1·23) and 18 kilos. of sulphuric acid (1·84 sp.gr.). Sometimes, red fumes were evolved only after some hours, but in presence of excess of green vitriol, they were always evolved at once and this gave the best colour. After standing for 24 hours, the mixture was suspended in a large quantity of cold water and allowed to settle. The washing by decantation was continued until the blue was free from sulphuric acid. It was then collected on linen filters, pressed into thin cakes, and cut up into cubes which were dried in the air and finally at 30°-40°. The yield was 39 to 39·5 kilos. of finished blue.

Another method was to treat the heated paste of ferrous ferrocyanides with ferric chloride, instead of with nitric acid, until the solution contained ferric in addition to ferrous salts, but according to Gentele, the cheapest and best method is to acidify the paste slightly with hydrochloric acid and pass chlorine gas into it until the solution shows a distinct ' ferric ' reaction with ferrocyanide.

From these descriptions it is clear that commercial Paris blue must contain, in addition to ordinary insoluble Prussian blue, one or more of the potassium ferric ferrocyanides. The presence of potassium appears to be of importance, a less satisfactory colour being produced when sodium ferrocyanide is used in its preparation. H. E. Williams says that potassium may be replaced by ammonium with satisfactory results. A. Eibner and L. Gerstacker (J. Soc. Chem. Ind. 1912, 31, 1041) state that the blues with a high potassium content possess the technically desirable greenish shade, those poor in potassium being dull with a violet tinge. They have found 12 p.c. K and 5·5 p.c. H_2O in ' steel-blue ' and ' bronze blue ; ' 9 p.c. K and 10·5 p.c. H_2O in ' Paris blue,' the lowest value found in a commercial blue being 1·5 p.c. K and 24 p.c. H_2O. In the commercial pigments, Paris blue is diluted with starch, heavy spar, gypsum, zinc white, or burned and finely ground kaolin. The white admixture, after having been ground very finely by itself, is added to the Paris blue paste, and along with it passed through a colour mill. Very low qualities of

blue are faced by rotating the dry cubes in a cask with the fine dust of pure Paris blue.

Potassium ferrocyanide (yellow prussiate of potash, *Blutlaugensalz*, Ger.) crystallises from aqueous solutions in large, well-formed, orange-yellow tetragonal pyramids of the composition $K_4Fe(CN)_6,3H_2O$; sp.gr. 1·86. The crystals do not change when exposed to the air at ordinary temperatures. They begin to lose water at 60°, and the finely powdered salt may be completely dehydrated at 100°, forming a white powder which begins to decompose, in absence of oxygen, slightly below a red heat to a mixture of potassium cyanide, carbon and iron, nitrogen escaping. The powder takes fire at a considerably lower temperature when heated in contact with air. It is insoluble in alcohol. The soluble ferrocyanides are completely decomposed by boiling with mercuric oxide

$$K_4Fe(CN)_6+3HgO+2H_2O$$
$$=3Hg(CN)_2+FeO+4KOH$$
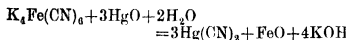
They are also decomposed by aurous cyanide, hydroxide, and even by finely-divided gold in the presence of oxygen

$$3Au+K_4Fe(CN)_6+2H_2O+O_2$$
$$=3KAu(CN)_2+Fe(OH)_3+KOH$$
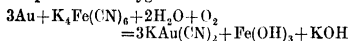
(E. Beutel, Zeitsch. anorg. Chem. 1912, 78, 141). According to Etard (Ann. Chim. Phys. 1894, [7] 2, 546), the solubility, expressed in grams of anhydrous salt dissolved by 100 grams of water, is 14·5 at 0°, 24·5 at 20°, 36 at 40°, 49·5 at 60°, 64 at 75°, 70 at 80°, 72 at 89°, 74 at 98°, and 88 at 157°. The salt is much less soluble in solutions of potassium salts. The specific gravity of the aqueous solutions is given below (Schiff, Annalen, 1860, 113, 199) :—

Grs. $K_4Fe(CN)_6,3H_2O$ per 100 grs. of solution	1	5	10	15	20
Sp.gr. at 15°	.	1·0058	1·0295	1·0605	1·0932 1 1275

Sodium ferrocyanide crystallises in large lemon-yellow monoclinic prisms or rhombohedra of the composition $Na_4Fe(CN)_6,10H_2O$ (Conroy, J. Soc. Chem. Ind. 1898, 17, 103), which are permanent when exposed to the air at the ordinary temperature, but are completely dehydrated at a little above 100°. The behaviour of the dry salt, when heated, resembles that of the potassium compound. The solubility in water (Conroy, J. Soc. Chem. Ind. 1898, 17, 103): grams anhydrous salt dissolved by 100 grams of water, is at 20°, 17·9; at 30°, 23·5; at 40°, 29; at 50°, 35·5; at 60°, 42·5; at 70°, 51·5; at 80°, 59·2; at 90°, 61; and at 100°, 63.

Zinc ferrocyanide $Zn_2Fe(CN)_6,6H_2O$ is a white amorphous substance obtained by the action of calcium or hydrogen ferrocyanide on an excess of zinc chloride in aqueous solution. With other soluble ferrocyanides the precipitate contains more or less of the metal of the ferrocyanide used, a fact referred to in more detail in the analytical section of this article. It is insoluble in dilute acids, completely soluble in caustic alkalis to a mixture of ferrocyanide and zincate, and only partially decomposed by alkali carbonates.

Potassium ferricyanide, red prussiate of potash, $K_3Fe(CN)_6$, was discovered by Leopold Gmelin in 1822. He prepared it by passing chlorine into a solution of potassium ferro-

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cyanide until it no longer gave a blue colour with a ferric salt :

$$2K_4Fe(CN)_6+Cl_2=2K_3Fe(CN)_6+2KCl$$
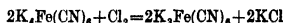
The salt is always manufactured by this reaction; the ferrocyanide is sometimes used in the form of a dry powder, in which case a mixture containing potassium chloride is obtained. Most commonly, a cold 10 p.c. solution of potassium ferrocyanide is treated with chlorine until conversion is just complete. A little Prussian green is always formed by the action of chlorine on the ferricyanide, and as this passes through any filter it spoils the appearance of the product. The difficulty may be avoided by evaporating the solution to crystallisation and then adding a little caustic potash which decomposes the green into ferric hydroxide, which is easily removed by filtration, and potassium ferrocyanide, which is apt to crystallise out along with the ferricyanide. The yield of ferricyanide, in this process, is 85 to 90 p.c. of the theoretical quantity.

A. W. Williamson (Annalen, 1846, 57, 225) found that potassium ferric ferrocyanide (Williamson's blue), when boiled with potassium ferrocyanide, gives potassium ferricyanide and Everitt's salt

$$K_4Fe^{II}(CN)_6+KFe^{III}[Fe^{II}(CN)_6]$$
$$=K_3Fe^{III}(CN)_6+K_2Fe^{II}[Fe^{II}(CN)_6]$$
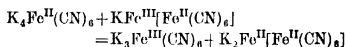
Since Everitt's salt is readily oxidised to Williamson's blue by warming with dilute nitric acid, the process might (as Dittmar suggested) be utilised to complete the conversion of ferro- into ferricyanide, chlorine being used up to the point at which Prussian green begins to be formed.

Many other oxidising agents have been suggested in place of chlorine, such as bromine, lead peroxide, calcium plumbate, potassium permanganate and persulphate, and electrolytic oxidation (*see* Bertelsmann, Technologie der Cyanverbindungen).

Potassium ferricyanide crystallises from water in magnificent, deep-red, monoclinic prisms which may be very large. It is anhydrous; sp.gr. 1·845. The aqueous solution has an intense yellow colour. The solubility (grams of anhydrous salt dissolved by 100 grams of water) is 33 at 4·4°, 36 at 10°, 40·8 at 15·5°, 58·8 at 37·8°, 77·5 at 100°, and 82·6 at 104·4° (Wallace, Dingl. poly. J. 1856, 142, 52). Specific gravity of the solutions at 15° (Schiff, Annalen, 1860, 113, 199) :—

Per cent. $K_3Fe(CN)_6$	1	5	10	15	20	25	30
Sp.gr.	1·0051	1·0261	1·0538	1·0831	1·1139	1·1462	1·1802

The aqueous solution is decomposed by light, potassium ferrocyanide being formed. The caustic alkaline solution is a strong oxidising agent which decolourises indigo instantaneously. The alkaline solution is also reduced by hydrogen peroxide, oxygen being evolved.

Ferric ferricyanide. The dark-brown solution, formed when solutions of a ferricyanide and of a ferric salt are mixed, contains ferric ferricyanide in the form of a highly disperse colloid. Ultramicroscopic examination show that the particles gradually increase in size, a green substance ultimately separating out

2 G

(R. Haller, Kolloid Zeit. 1917, 20, 76). The formation of a green substance by the action of chlorine on potassium ferricyanide was first noticed by Pelouze (Ann. Chim. Phys. 1838, [2] 69, 40). Green ferric ferricyanides are also obtained by boiling Prussian blue with strong nitric acid or by precipitating potassium ferricyanide containing a little ferrocyanide with ferric chloride (H. E. Williams).

Potassium carbonylferrocyanide

$$K_3[Fe(CN)_5CO]H_2O$$
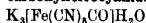
is formed by the action of carbon monoxide on an aqueous solution of potassium ferrocyanide at 135°

$$K_4Fe(CN)_6 + CO + 2H_2O$$
$$= K_3Fe(CN)_5CO + NH_3 + KHCO_2$$
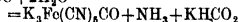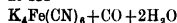
(Müller, Ann. Chim. Phys. 1889, [6] 17, 94). Carbonylferrocyanides are found in the cyanide mud and spent oxide of the gas works, in which from 2 to 5 p.c. of the cyanogen (exceptionally as much as 20 p.c.) is present in this form (H. G. Colman, Analyst, 1908, 33, 261). When the caustic soda extract of these materials, mixed with 4 to 5 times its volume of methylated spirit, is allowed to stand for some hours, the sodium ferrocyanide crystallises out completely, leaving the carbonyl ferrocyanide in solution. It is isolated, in the form of the amorphous, deep-violet ferric salt, by adding ferric chloride to the acidified solution. The deliquescent calcium salt $Ca_3[Fe(CN)_5CO]_2,8H_2O$ is obtained by boiling the ferric salt with milk of lime. The carbonyl ferrocyanides resemble the corresponding ferrocyanides, but are paler in colour and more soluble in water. The copper salt, is a green precipitate soluble in excess of ammonia, is characteristic.

Sodium nitroprusside

$Na_2[Fe(CN)_5NO]\cdot2H_2O$ was first prepared by Lyon Playfair (Phil. Mag. 1850, [3] 36, 197) by the action of dilute nitric acid on a solution of a ferrocyanide. The primary products of the change, hydroferricyanic acid and nitric acid, react thus: $H_3Fe(CN)_6 + NO = H_4Fe(CN)_5NO + HCN$. The salt is also formed by adding a concentrated solution of ferrous sulphate to a solution containing equal parts of sodium nitrite and potassium cyanide. It crystallises in dark-red prisms, soluble in 2½ parts of water at 16°. The solution is not precipitated by a ferric salt, and gives a deep violet colouration with alkali sulphides.

### Sodium aquopentacyanoferroate

$$Na_3[Fe(CN)_5H_2O],5H_2O$$
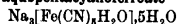
is obtained by the action of reducing agents, such as phenylhydrazine or hydroxylamine, or of oxidising agents, such as potassium hypobromite and hydrogen peroxide on a solution of sodium nitroprusside at temperatures below 0°. The action of hydrogen peroxide is analogous to its behaviour with a ferricyanide

$$2K_3Fe(CN)_6 + H_2O_2 + 2KOH$$
$$= 2K_4Fe(CN)_6 + O_2 + 2H_2O$$
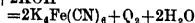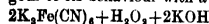
The salt crystallises in reddish-yellow needles, giving an intensely yellow solution, which does not yield a violet colouration with alkali sulphides.

Sodium aquopentacyanoferriate

$$Na_2[Fe(CN)_5H_2O]$$
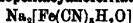
is obtained by oxidising the foregoing compound with bromine. It is a deep violet-blue substance,

and Cambi has shown that the potassium perferricyanide obtained by Bong (Bull. Soc. chim. 1875, [2] 24, 268) and Skraup (Annalen, 1877, 189, 368) by the action of potassium chlorate and an acid on a solution of potassium ferricyanide, is the potassium salt of the same acid. It is also obtained by the action of excess chlorine on potassium ferricyanide, a deep violet solution being formed, from which the salt is precipitated by alcohol.

A series of pentacyano iron compounds has also been prepared, which may be regarded as derived from the aquo-compounds just described by the replacement of the H_2O group in the anion by one of the groups NO_2, AsO_2, SO_3, NH_3, or substituted ammonias.

Literature.—K. A. Hofmann, Zeitsch. anorg. Chem. 1896, 11, 31, and 278; *ibid.* 1896, 12, 146; Annalen, 1900, 312, 1; W. Manchot, Ber. 1912, 45, 2869; L. Cambi, Gazz. chim. ital. 1911, 41, i. 157.

Hexamethyl carbylamine ferro salts

By the action of methyl sulphate on dry potassium ferrocyanide or of methyl iodide on silver ferrocyanide, E. G. J. Hartley has obtained a series of salts of the general formula $[Fe(CNCH_3)_6]R_2$, R being a univalent acid radical, in which the iron cyanogen complex plays the part of cathion. When heated with concentrated sulphuric acid, or boiled with aqueous caustic soda, these salts are decomposed, the whole of the nitrogen appearing in the form of methylamine, or of methyl carbylamine, which proves that all the nitrogen atoms are linked to methyl.

Tetramethyl ferrocyanide $\left[Fe\frac{(CNCH_3)_4}{(CN)_2}\right]$ is

formed when hexamethylcarbylamine ferrochloride $[Fe(CNCH_3)_6]Cl_2$ is heated at 140°–150° in a vacuum for 6–9 hours, methyl chloride being split off. Two isomeric forms, with the same molecular weight, have been separated from the reaction product. The α-isomer is much more readily soluble in water, alcohol, and chloroform than is the β-isomer, and from water it crystallises with two molecules of water of crystallisation, the β-isomer combining with six. They also differ in their behaviour towards methyl iodide, with which the α-compound combines at 100°, yielding hexamethylcarbylamine ferroiodide, the β-compound remaining unchanged. No method of converting the one form into the other has been discovered (E. G. J. Hartley, Chem. Soc. Trans. 1910, 1066 and 1725; *ibid.* 1911, 1549; *ibid.* 1912, 705; *ibid.* 1913, 1196).

Constitution of the Iron Cyanogen Compounds. —When dissolved in water these compounds dissociate electrolytically into a complex ion containing the iron, cyanogen, and other groups; the sign and magnitude of the electric charge of this ion depend on the nature of its constituent groups of atoms. The ions $Fe(CN)_6'''$, $Fe(CN)_6''''$, $Fe(CN)_5CO'''$, $Fe(CN)_5NO''$, $Fe(CNCH_3)_6''$ are examples of this. These ions possess considerable stability, and are probably dissociated to a very small extent. For example, the ferrocyanogen ion is supposed to dissociate thus, $Fe(CN)_6'''' \rightleftharpoons Fe'' + 6(CN)'$ (F. Haber, Zeit. Elektrochem. 1905, 11, 846; Foster, Chem. Soc. Trans. 1906, 912). In the dark the concentration of ferrous ion is too small to produce

a precipitate of FeS with an alkali sulphide, but the complete decomposition of the ferrocyanogen complex by mercuric oxide shows that the minute concentration of (CN)′ in a solution of a ferrocyanide is greater than that in a solution of mercuric cyanide. The dissociation of the ferrocyanogen ion is increased by light, especially the ultra-violet rays, so that in alkaline solutions, oxygen produces a precipitate of ferric hydroxide. The increased dissociation is, however, so small that no appreciable increase in the conductivity of the solution can be detected.

Measurements of the osmotic pressure and electrical conductivity of solutions of the ferrocyanides of calcium and strontium have been made by the Earl of Berkeley, Hartley and Stephenson (Phil. Trans. 1909, 209A, 319), the results of which are incompatible with the assumption of a molecule $Ca_2[Fe(CN)_6]$ dissociating into three ions, it is suggested that the undissociated molecules may be double. The non-electrolyte, tetramethyl ferrocyanide, exists as single molecules in aqueous solution, and, from measurements of the freezing-point, Buchböck (Zeitsch. phys. Chem. 1897, 23, 157) arrived at the same result in the case of tetraethyl ferrocyanide.

Several cases of isomerism have been recorded. Locke and Edwards (Amer. Chem. J. 1899, 21, 193 and 413) observed that the ordinary anhydrous, red potassium ferricyanide is converted into a greenish-yellow modification, crystallising with 1 molecule of water by treatment with acids. This β-ferricyanide gives no precipitate with bismuth nitrate, the ordinary α-modification giving a straw-coloured precipitate. The β-ferricyanide is converted into the α-salt by treatment with alkalis. Briggs (Chem. Soc. Trans. 1911, 1019) describes similar behaviour on the part of the ferrocyanides. Faintly acid solutions deposit more deeply coloured crystals of the β-isomer, which are readily converted into the α-form by treatment with potassium cyanide or alkalis. The *l*-menthyl ammonium salts of the two isomers have different specific rotatory powers in alcoholic solution, otherwise only minute differences in density and solubility were observed. Bennett (Chem. Soc. Trans. 1917, 490) finds that the α- and β-ferrocyanides are crystalographically identical, and explains the difference of colour by slight decomposition of the acid solutions.

In addition to the isomeric tetramethyl ferrocyanides already mentioned, Hartley (Chem. Soc. Trans. 1914, 521) has recorded the existence of two isomeric trimethyl cobalticyanides $Co(CNCH_3)_3(CN)_3$ (attempts to prepare the ferricyanide derivative were unsuccessful), which differ considerably in solubility.

The synthesis of ferrocyanides from a ferrous compound and of ferricyanides by boiling excess of ferric hydroxide with an alkali cyanide (Skraup, Annalen, 1877, 189, 376), show that these compounds and their direct derivatives contain divalent and trivalent iron respectively. It is to be remembered that the iron cyanogen compounds here considered form one group of a great family of complex salts. Substances of the general formulæ
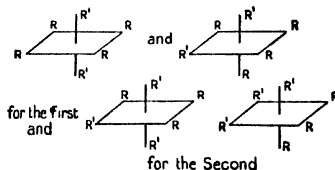
$$[M(CN)_6]R_3 \text{ and } [M(CN)_6]R_4$$
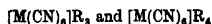
are known in which the metal is Co, Cr, Mn, Ru, Rh, Ir, and Os, and in which the CN group may be replaced by SCN. These are closely related in structure and chemical behaviour to large groups of metal ammonia and halogen complex salts. Under the circumstances, Werner's formulation of these salts, although it lacks the definiteness of the structural formulæ of organic chemistry, appears to be the best available. A. Werner (Neuere Anschauungen auf den Gebiete der anorganischen Chemie, 3rd ed. 1913) regards the complex salts as built up by the co-ordination of a maximum number of six groups of atoms round a central atom; carbon, nitrogen, and boron are exceptional, their maximum co-ordination number being four. The six groups are arranged symmetrically; at the angles of a regular octahedron, they are attached to the central atom, partly by the ordinary principal valencies, partly by secondary valencies. The nucleus so formed acts as a more or less stable whole, which may still be able to combine with other atoms at a greater distance from the centre or on an outer sphere. These more loosely held atoms dissociate electrolytically when the substance is dissolved; whether they are attached to the nucleus as a whole or to any particular atom in it is left undecided, although Werner inclines to the former view. The number and nature of the ionogenic groups depends on the nature of all the atoms included in the nucleus. For example, among the compounds described, we have :—

Ferro-series	Ferri-series	Complex forms
$[Fe(CN)_6]K_4$	$[Fe(CN)_6]K_3$	anion
$\left[Fe\genfrac{}{}{0pt}{}{(CN)_5}{CO}\right]K_3$	$\left[Fe\genfrac{}{}{0pt}{}{(CN)_5}{NO}\right]K_2$	anion
$\left[Fe\genfrac{}{}{0pt}{}{(CNCH_3)_4}{(CN)_2}\right]$	$\left[Co\genfrac{}{}{0pt}{}{(CNCH_3)_3}{(CN)_3}\right]$	not dissociated
$[Fe(CNCH_3)_6]Cl_2$		cathion

A further consequence of the theory is that complexes of the formulæ $\left[M\genfrac{}{}{0pt}{}{R_4}{R'_2}\right]$ and $\left[M\genfrac{}{}{0pt}{}{R_3}{R_3}\right]$ should exist in the two stereoisomeric forms represented by :

for the first and

for the Second

Possibly Hartley's isomeric tetramethyl ferrocyanide and trimethylcobalticyanides are examples of these forms of isomerism. Werner classifies the (somewhat uncertain) isomerism of the ferro- and ferricyanides as unexplained; but as Briggs has remarked (Chem. Soc. Trans. 1908, 1564), they would also come under the above heading if the potassium atoms are supposed to be attached to definite CN groups in the nucleus.

Manufacture of Potassium and Sodium Cyanides.—The methods of manufacture of these salts are most conveniently described together, since most of the processes used may equally well

be applied to making either salt. The most important technical processes have already been mentioned in the introduction to this article.

*Manufacture from Yellow Prussiate.*—Potassium cyanide was first prepared by Berzelius's method, which consists in heating dry potassium ferrocyanide to redness, when it decomposes thus : $K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$. The loss of cyanogen, which occurs in this way, is partly avoided by fusing the ferrocyanide with potassium carbonate, as first described by F. and E. Rodgers (Phil. Mag. 1834, [3] 4, 91). Liebig showed that the product contains cyanate, formed thus :

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2$$
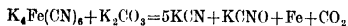
The fused salt is allowed to stand until the iron and carbon have settled out, and is then poured off into moulds. The comparatively small quantities of cyanide, which were used in electro-plating and for other purposes up to about 1890, were made by this process. The product was sold in white, porcelain-like cakes, containing from 30 to 70 p.c. of KCN.

In 1876, E. Erlenmeyer (Ber. 1876, 9, 1840) pointed out that a very pure product, containing on the average 40 p.c. of CN (equivalent to 100 p.c KCN), was obtained by fusing dry prussiate with metallic sodium in the proportions required by the equation

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$$
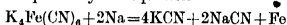
This process was taken up first by the Deutsche Gold and Silber Scheide-Anstalt (F. Roessler, V. Inter. Kongress für Angewandte Chemie, Berlin, 1903, 1, 638) in Frankfort-on-Main, in 1890 ; they obtained a practically quantitative yield by filtering off the spongy iron from the fused cyanide and pressing the iron while red hot. The cyanide so obtained is cast in cakes and forms a pure white crystalline mass. Since about 1905, sodium ferrocyanide has been used in this process in place of the potassium salt, and the product is almost pure sodium cyanide. The excess of the gas works ferrocyanide over that required in the colour industries is converted into sodium cyanide in this way.

It has been proposed to distil ferrocyanides with acids and to absorb the hydrocyanic acid in solutions of caustic alkalis. Grossmann (Eng. Pats. 36 and 4513, of 1903 ; J. Soc. Chem. Ind. 1903, 22, 1327) distils sodium ferrocyanide with 20 p.c. sulphuric acid in lead stills. the Everitt's salt remaining is re-converted into sodium ferrocyanide by boiling it with caustic soda in a current of air. The use of calcium ferrocyanide, which readily yields two-thirds of its hydrocyanic acid, was proposed by J. H. Paul (Eng. Pat. 72 of 1903). W. Feld (Eng. Pat. 24920 of 1901) converts insoluble ferrocyanides into mercuric cyanide, and then distils this with an acid. Dewrance and Williams (Eng. Pat. 28074 of 1908) distil the ferrocyanide, either soluble or insoluble, with 2-3 p.c. of its weight of cuprous chloride and a small excess of sulphuric acid, the whole of the hydrocyanic acid being evolved. None of these proposals is at present of technical importance.

The processes of Siepermann and Beilby were the first synthetic processes to produce cyanide in large quantities ; they are most conveniently considered together because, although they differ widely in the methods adopted in carrying them out, they are both based on the same chemical reaction which was also used by Scheele in the first synthesis of a cyanide ever made.

In Siepermann's process (D. R. P. 38012, March 10, 1886 ; Eng. Pat. 13697 of 1889 ; 9350 and 9351 of 1900) a dry mixture of about 2 parts of charcoal and 1 part of potassium carbonate—that is, a sufficient excess of charcoal to keep the mixture in the form of a dry unfused mass throughout the process—is heated in the upper part of a vertical iron tube to a dark-red heat and treated with dry ammonia gas, which is taken up, forming potassium cyanate. The product is then allowed to fall into the lower end of the tube, which is heated to bright redness At the higher temperature the cyanate is converted into cyanide, the carbon monoxide evolved escaping through the upper part of the tube along with the hydrogen formed from the ammonia, without taking any part in the reaction. The finished material is drawn off into air-tight receptacles where it is allowed to cool completely, after which it is systematically lixiviated with water. Potassium cyanide may be precipitated from the solution obtained (sp.gr about 1·4) by adding excess of potassium carbonate, but according to the later patents it is preferable to evaporate it almost to dryness and extract the unchanged potassium carbonate with small quantities of water at 66°. The residue of potassium cyanide and cyanate is then treated with water between −18° and +5°, which dissolves the cyanide and any residue of carbonate, leaving almost pure potassium cyanate. The product of this process was first put on the market in 1892 (G. Beilby, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 630), but as the substance was in the form of a damp deliquescent mass, it could not be exported for use at the mines by itself but had to be fused with the product of the ferrocyanide process.

In the Beilby process (Eng. Pat. 4820 of 1891), which began to produce in the same year, the quantity of charcoal used is very much smaller, very little more being employed than is necessary to convert the potassium carbonate into cyanide thus :

$$K_2CO_3 + 4C + 2NH_3 = 2KCN + 3CO + 3H_2$$
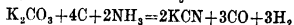
The charcoal is added gradually during the progress of the operation, so that the material is always in the form of a fused liquid through which the ammonia gas is forced under some pressure. This is continued until a sample shows the conversion to be sufficiently complete ; it is then only necessary to separate the small excess of charcoal by filtration in order to have a pure white saleable product. Since the melting-point of pure potassium carbonate (890°) is inconveniently high, previously made cyanide was mixed with it in starting the process, or the more readily fusible mixture of sodium and potassium carbonates was used, so that the cyanide made by the process was very similar in composition to that produced by the Erlenmeyer process from potassium ferrocyanide. In 1899 the Beilby process contributed fully one-half of the total European production of cyanide.

It is difficult to obtain a satisfactory yield on the ammonia in these processes, owing to the rapidity with which it decomposes into its

elements at temperatures above 500° and in contact with metals, especially iron (Ramsay and Young, Chem. Soc. Trans. 1884, 88; Beilby and Henderson, *ibid.* 1901, 1245). For this reason it is necessary to work at the lowest possible temperature. Siepermann, for example, obtained a yield of 86 p.c. on the ammonia when it was absorbed at a dark-red heat, but only 58 p.c. at a bright cherry-red heat. Readman (J. Soc. Chem. Ind. 8, 757, 1889) showed that almost theoretical efficiencies can be obtained at the low temperatures attainable in an ordinary organic combustion furnace; whilst Conroy (*ibid.* 15, 12, 1896), working at very high temperatures (1000°–1200°), could not get more than 30 to 33 p.c. of the ammonia in the form of cyanide. In practice the reaction velocity is also of great importance; in the Beilby process, where the advantage of the large surface exposed by Siepermann's dry mass of alkalised charcoal is sacrificed, the reaction is too slow at temperatures below 900°, the best results are obtained at 980°. In order to keep down the dissociation of the ammonia at this high temperature it is injected into the fused mixture through copper-lined tubes of such diameter that its time of contact with the hot metal is less than one-tenth of a second.

The chemistry of the reaction has been investigated by J. Pfleger (F. Roessler, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 638). Ammonia and potassium carbonate react, yielding potassium cyanate and hydroxide, a carbamate being most probably formed as an intermediate product:

$$CO(OK)_2 + NH_3 = CO{<}^{NH_2}_{OK} + KOH$$

$$CO{<}^{NH_2}_{OK} = KCNO + H_2O$$
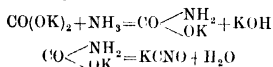
When pure potassium cyanate is heated at 800°–900°, it decomposes, cyanide and carbonate being formed and nitrogen, carbon dioxide, and carbon monoxide evolved. The mechanism of this change is probably as follows: Drechsel (J. pr. Chem. 1877, [2] 16, 201.) has observed that the cyanates of the alkaline earth metals decompose, when heated, into carbon dioxide and the corresponding cyanamide salts. Assuming that the alkali cyanates behave similarly, the first change will be

$$2KCNO = K_2CN_2 + CO_2$$
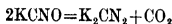
Potassium cyanamide, however, decomposes completely at lower temperatures than 800° into cyanide, potassium, and nitrogen:

$$K_2CN_2 = KCN + K + N$$

The carbonate and carbon monoxide observed are thus due to the reaction between the metallic potassium and carbon dioxide which are formed simultaneously. In presence of charcoal in excess, the greater part of the cyanamide follows Drechsel's reaction (J. pr. Chem. 1880, [2] 21, 77), $K_2CN_2 + C = 2KCN$, instead of decomposing; so that the apparent reduction of cyanate by carbon probably takes place in the two stages:

$$2KCNO = K_2CN_2 + CO_2$$
$$\text{and } K_2CN_2 + C = 2KCN$$
$$CO_2 + C = 2CO$$
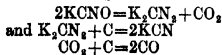
The reactions occurring in the Beilby process are the same, except that, the whole process

being carried on at the higher temperature, the formation of cyanate and its conversion into cyanide take place simultaneously instead of being more or less sharply separated as they are in Siepermann's process.

In the Siepermann process, it is easier to use the ammonia efficiently, owing to the lower temperature employed, but this is counterbalanced by the greater difficulty of working up the product into a marketable form.

The Castner Process.—In 1894 H. Y. Castner (Eng. Pat. 12219 of 1894) patented a process in which sodium was fed in at the upper end of a column of red-hot charcoal through which a current of dry ammonia gas was passed from below, the reaction being expressed by the simple equation:

$$2Na + 2C + 2NH_3 = 2NaCN + 3H_2$$
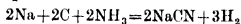
In a second patent (H. Y. Castner, Eng. Pat. 21732, 1894) it is shown that better results are obtained by first allowing the sodium and ammonia to react at a low temperature (300° to 400°), forming sodium amide $NaNH_2$, and then running the amide on to an excess of red-hot charcoal with which it reacts thus:

$$NaNH_2 + C = NaCN + H_2$$
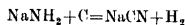
Working in this way, it happened on one occasion that an excess of amide was accidentally run into the vessel containing the charcoal, and a product of unusual appearance was obtained, in which the writer found a large quantity of sodium cyanamide. The reaction, therefore, takes place in three stages, in which the nitrogen enters successively into more and more stable combinations. First sodium amide is produced, a compound which begins to decompose rapidly into its elements at 500° (Titherley, Chem. Soc. Trans. 1894, 504); this reacts either with carbon

$$2NaNH_2 + C = Na_2CN_2 + 2H_2$$
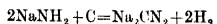
or, as Pfleger found, with sodium cyanide

$$NaNH_2 + NaCN = Na_2CN_2 + H_2$$
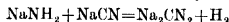
forming sodium cyanamide, a compound which only decomposes slowly at 600°, and finally this takes up carbon, forming sodium cyanide which is quite stable at any temperature attained in the process.

Like the Beilby process, this process yields a fused product containing very small quantities of solid impurities which are easily removed by filtration. After being cast in iron moulds, the cyanide is obtained in the form of pure white cakes with crystalline fracture, containing 97¼ to 98 p.c. of NaCN (equivalent to 129–130 p.c. of KCN).

The greater part of the world's cyanide requirements has been from its inception to the present date, 1920, supplied by this process in England. It was worked out, under Mr. Castner's direction, at the works of the Aluminium Co. at Oldbury; the first manufacturing plant was erected, by the writer, at Frankfurt-on-Main, just before Mr. Castner's death in 1899, and the second at Glasgow in 1900. The experienced assistance of the staffs of the Frankfurt and Glasgow companies led to rapid improvement of working details. A third installation started work near New York in 1901.

'*Schlempe*' *Process.*—The juice of the sugar beet contains both inorganic and organic substances other than sugar, and these substances accumulate in the molasses. In Germany, rather more than half of the molasses made are treated with strontia, which combines with the sugar to form an insoluble sucrate; the residue left after removing this, the concentrated essence of the impurities of the original juice, is known as 'schlempe.' After concentration to sp.gr. 1·4, it contains 75 p.c. of dry substances, 30 p.c. of which are inorganic (mainly potassium) salts and the remainder organic substances. The 'schlempe' contains about 4 p.c. of nitrogen in the form of betaïne

$$CH_2—CO$$
$$\underset{N(CH_3)_3}{|} >O$$

and decomposition products of the vegetable proteïns. Of the molasses not treated by the strontia process, a large part is consumed as cattle food and a small part fermented to alcohol. The residue of the alcoholic fermentation is known in France as '*vinasses.*'

The first attempt to utilise the nitrogen of 'vinasses' was made by Vincent in 1877–1880. He distilled the 'vinasses' in horizontal iron retorts at a red heat, ammonia, a mixture of the three methylamines, monoethyl-, mono-butyl, and monopropylamines, methyl alcohol, and combustible gases was evolved, and potassium carbonate mixed with some carbon remained behind (E. Duvillier and A. Busine, Ann. Chim. Phys. 1881, [5] 23, 289; H. Ost, Zeitsch. angew. Chem. 1906, 19, 609). In 1879 Ortlieb and Müller devised a process for converting Vincent's methylamines into hydrocyanic acid, which was worked by the Société Anonyme de Croix (Eng. Pat. 3844, of 1879). The vapour of the methylamines was passed through a red-hot retort, yielding ammonia, hydrocyanic acid, methane, and hydrogen. The ammonia was absorbed by sulphuric acid, and the hydrocyanic acid by a suspension of ferrous hydroxide in caustic potash. The manufacture of the methylamines was abandoned in 1881 for want of a market, and with it the production of cyanides.

The problem was again attacked by Bueb (Reichardt and Bueb, Eng. Pat. 7171 of 1895; Bueb, Eng. Pat. 26259 of 1898). Instead of separating the products of distillation of the 'schlempe,' he passed them directly, after condensing some tar, into a series of firebrick channels which were heated to bright redness. The ammonia and hydrocyanic acid were absorbed together in a solution of ferrous sulphate, and the product worked up in the same way as that made in the gas-works. The narrow flues were soon stopped up by deposits of carbon, so that they were replaced by chambers filled with fire-brick checker-work, which is heated up to 1000° by firing directly with producer gas; during this process, the deposit of carbon is burned. Two such chambers are used alternately, the one being heated up whilst the gases from the retorts are passing through the other. The gases leaving the decomposing chambers contain 7 p.c. HCN; 7 p.c. NH₃; 8 p.c. (mainly) CH₄; 12 p.c. H₂; 18 p.c. CO; 24 p.c. CO₂; and 24 p.c. N₂. In passing through the decomposing

chamber, the methylamines disappear and hydrocyanic acid is formed, the ammonia undergoing but little change. The ammonia is now removed from the gas by absorption in sulphuric acid, and the hydrocyanic acid absorbed in water in a suitable column. The solution of hydrocyanic acid is then distilled into a solution of caustic soda (A. Vasseur, Bull. Soc. Ind. Nord de la France, 1913, 41, 445). The solution of sodium cyanide is evaporated to crystallisation, the crystals dried, and briquetted by compressing them into blocks which are dried at 70° *in vacuô* (Eng. Pat. 18096, of 1907), and then contain sodium cyanide equivalent to 120 p.c. of KCN.

Of the nitrogen in the 'schlempe,' about one-half is converted into nitrogen gas and so lost; a quarter is obtained as sodium cyanide and the remainder as ammonium sulphate.

The decomposition of di- and tri-methyl-amine, when passed through a heated porcelain tube filled with fragments of porcelain, fire-brick, or charcoal, has been studied by Voerkelus (Dissertation, Hannover, 1909). At temperatures lying between 800° and 1000°, as much as 98 p.c. of the trimethylamine decomposes into hydrocyanic acid and methane $N(CH_3)_3 = HCN + 2CH_4$, the remaining 2 p.c. yielding ammonia $N(CH_3)_3 + 3H_2 = NH_3 + 3CH_4$. This result was obtained when the gaseous contents of the tube were changed once in 7½ seconds; with a slower current of gas and also with a contact material of large surface (fireclay or charcoal) or with iron, a part of the hydrocyanic acid is decomposed into its elements. The rate of decomposition at 1000°, however, is small. At 720° the yield of hydrocyanic acid was only 78 p.c., and at 600° none was produced.

The formation of hydrocyanic acid from dimethylamine also begins between 600° and 700°, from 800° to 1100° the change takes place quantitatively in accordance with the equation $NH(CH_3)_2 = HCN + CH_4 + H_2$. If hydrogen is present, however, a second change occurs $NH(CH_3)_2 + 2H_2 = NH_3 + 2CH_4$. Using equal volumes of hydrogen and dimethylamine, this reaction is of no importance, but as the hydrogen present increases more and more of the dimethylamine is converted into ammonia until, with a mixture of 97 parts of hydrogen to 3 parts of dimethylamine, ammonia is the sole product.

The behaviour of monomethylamine is probably analogous to that of dimethylamine. A. Wurtz (Ann. Chim. Phys. 1850, [3] 30, 443) found that, at a red heat, it decomposes in accordance with the equation :

$$3CH_3.NH_2 = 2HCN + NH_3 + CH_4 + 3H_2$$
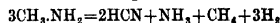
In practice, therefore, the losses of hydrocyanic acid and ammonia by decomposition will depend on the rate of passage of the gases and on the nature of the contact material—the deposit of carbon on the porous bricks diminishing the decomposition of hydrocyanic acid.

The Deutsche Gold und Silber Scheide Anstalt (Fr. Pats. 447725 and 448722 of 1912) has made practical application of these observations by passing the gases at a high velocity through heated conduits made of fused quartz or Dinas brick without filling material. By this means, it is said that practically the whole

of the nitrogen is obtained as ammonia or hydrocyanic acid.

Manufacture of Sodium and Potassium Cyanides from Sulphocyanides.—The sulphocyanide is first converted into ferrocyanide by one of the methods already described, and the ferrocyanide then worked up into cyanide; this is the method actually in use. Other more direct processes have been used to some extent.

The earliest of these was D. J. Playfair's process (Eng. Pat. 7764 of 1890). Playfair found that certain metals, lead and zinc especially, when fused with potassium sulphocyanide, abstract the sulphur, leaving potassium cyanide, which may be separated from the metallic sulphide by extraction with water. The fusion is carried out at 400°, and 70–80 p.c. of the sulphocyanide is converted into cyanide (D. J. Playfair, J. Soc. Chem. Ind. 1892, 11, 14; Conroy, *ibid.* 1896, 15, 8). The reaction is slower with lead, owing to the small surface offered by the fused metal, whilst with zinc the product is apt to be contaminated by the double cyanide of zinc and potassium. The process was worked about 1894 by the British Cyanides Co. at Oldbury (Brussels Exhib. 1910, Catalogue of British Chem. Section, p. 63).

Raschen's process (Eng. Pats. 10476, 10956, and 21678 of 1895 ; 19767 of 1898 ; 12180 of 1900) is based on the oxidation of sulphocyanic acid to hydrocyanic and sulphuric acids which was first observed by E. A. Hadow (Annalen, 1858, 108, 380). Hadow found that permanganate, lead peroxide, manganese dioxide, and nitric acid bring about the same reaction. Raschen found that it takes place quantitatively in acid solutions only when an excess of the oxidising agent is present. If the oxidising agent is added to the sulphocyanate, solid yellow compounds are produced of variable composition, one of which, 'canarin' (*q.v.*), has been used as a yellow dye.

The Raschen process (J. T. Conroy, J. Soc. Chem. Ind. 1899, 18, 432) was carried out by allowing a solution containing about 15 p.c. of sodium sulphocyanate to flow into dilute nitric acid kept at the boiling-point by means of live steam. The reaction :

$$NaCNS + 2HNO_3 = HCN + NaHSO_4 + 2NO$$

took place. From 3 to 5 p.c. of the nitric acid was less completely reduced, N_2O_3 being formed, so that the gases leaving the decomposer were first scrubbed with a little water. The resulting solution of nitric, nitrous, and hydrocyanic acids was returned to the decomposer. The gas, which now contained about 1 volume of hydrocyanic acid to 2 volumes of nitric oxide, was passed through a solution of caustic soda (sp.gr. 1·37), which absorbed the hydrocyanic acid. It was found necessary to avoid saturating this solution completely with hydrocyanic acid because of the brown decomposition products which are formed from the free acid in presence of a cyanide. The nitric oxide was then mixed with air and passed upwards through towers packed with flints down which water trickled ; in this way it was reconverted into nitric acid (sp.gr. 1·12) which was returned to the decomposer. The solution of sodium cyanide was evaporated to dryness in vacuum pans without appreciable loss.

The reduction of sulphocyanides by hydrogen was studied by Playfair (J. Soc. Chem. Ind. 1892, 11, 14). He found that hydrogen acts on potassium sulphocyanide at a dull-red heat, forming potassium cyanide and sulphide and sulphuretted hydrogen.

Conroy, Heslop, and Shores (J. Soc. Chem. Ind. 1901, 20, 320) showed that the reaction takes place slowly at 500°, and fairly fast at 600°. Their results indicate that two reactions occur simultaneously :

$$KSCN + H_2 = KCN + H_2S$$

and

$$2KSCN + 2H_2 = K_2S + 2HCN + H_2S$$
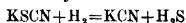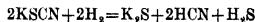
A little ammonia is also evolved, probably owing to the difficulty of drying the sulphocyanide completely. About 70 p.c. of the nitrogen is obtained in the form of cyanide and 20 p.c. as hydrocyanic acid. With barium and cuprous sulphocyanides, the reaction is similar to that represented by the second of the above equations, the principal nitrogenous product being hydrocyanic acid. With the cuprous salt, the reaction begins below 300°.

Rossiter, Crowther, and Albright (Eng. Pats. 4403 and 6226 of 1901) have patented a process based on the behaviour of the cuprous salt. It is mixed with finely divided copper and heated at temperatures rising from 150° to 650° in a current of hydrogen. Hydrocyanic acid is evolved and cuprous sulphide remains behind.

Synthesis of Cyanides from Uncombined Nitrogen.

Up to the outbreak of the European War in 1914 the nitrogen of cyanides was almost exclusively derived either from organic matters of animal origin or from coal. The persistent attempts to synthesise cyanogen compounds from atmospheric nitrogen, which date back to the first half of the nineteenth century, have been renewed during recent years, and important progress has been made. The deficiency of cyanide caused by war conditions has, to a small extent, been supplied by the product of one of the processes using atmospheric nitrogen ; but it remains to be seen whether any one of them will be able to hold its own in competition with the older sources of supply under more normal conditions.

The attacks on the problem of fixing free nitrogen in the form of cyanide have been made by several paths which sometimes intersect. For convenience of description, they may be arranged according to the raw materials used ; the action has been studied of nitrogen on :—

1 *a.* Alkali metal carbonates and carbon.
   b. Alkali metals and carbon.
   c. Barium carbonate and carbon.
2 *a.* Carbides of metals.
   b. Acetylene.
3. Metals forming nitrides, subsequently converted into cyanides.

1 a. *Action of Nitrogen on Alkali Metal Carbonates and Carbon.*

Scheele may have been the first to fix atmospheric nitrogen in the form of a cyanide. Writing in 1783, he says (Chemical Essays, 1901, reprint, 288) : ' We know that charcoal powder, brought into fusion with fixed alkalis, yields likewise a kind of lixivium sanguinis, though weak.' The

source of the nitrogen is, however, doubtful, since charcoal contains a little combined nitrogen. Desfosses (Ann. Chim. Phys. 1828, 38, 158) mentions that notable quantities of cyanide are obtained by the action of nitrogen on a mixture of potash and carbon heated to redness, but the first thorough investigation of the reaction was made by Lewis Thompson, who was awarded the Gold Isis Medal of the Society of Arts, in 1838, for his improvements in the manufacture of Prussian blue. The chief improvement consisted in the substitution of atmospheric nitrogen for that contained in animal matters (Mechanics Magazine, 1839, 31, 92). Potash (2 parts), coke (2 parts), and iron turnings (1 part), were ground together to a coarse powder and heated in an open crucible, for half an hour, to a full red heat with occasional stirring; the end of the operation was indicated by the cessation of the jets of purple flame which arose from the surface of the mixture. After cooling, the material was lixiviated, and Prussian blue precipitated in the usual way. The yield was better with larger quantities of material than it was with smaller batches; thus 6 oz. of pearlash, containing 45 p.c. K₂O, yielded 0·62 oz. (295 grams) of Prussian blue, whilst 12 oz. (1 lb.) of the same material yielded 2·8 oz. (1355 grams) of blue; [1] that is, 0·23 and 0·54 part of Prussian blue for 1 part of K₂O used. Assuming that the Prussian blue was dried at 30°–40°, and contained 28 p.c. of water, the theoretical yield is 2·1 parts, so that Thompson cyanised from 11 to 26 p.c. of the potash used. This calculation may underestimate the yield, because it is stated that the Prussian blue spoken of is the 'pure perferrocyanate of iron.' Coke was used (because wood charcoal burns away too quickly), and the 'carbonaceous matter may be worked over again many times, and is even improved by each operation.' The importance of the addition of iron is insisted on; when it is not employed a much higher temperature is required.

The importance of Thompson's discovery of the catalytic action of iron was not fully appreciated for nearly three-quarters of a century, perhaps because the addition of iron for an entirely different purpose was a familiar feature of the current process of manufacture of ferrocyanide. Contemporary criticism was concerned mainly with the source of the nitrogen, although Thompson's statement that the carbonaceous matter improves on re-use would, if confirmed, have put the matter beyond doubt.

G. Fownes, in a paper read to the British Association (The Chemist, 1841, 2, 261), insisted on the possible error due to the presence of nitrogen in the coke used, and found, like Scheele, that charcoal or coke yields 'abundance of cyanide' when heated with potash in a closed crucible at a moderate red heat, which is not the case when pure carbon is used. When pure nitrogen was passed over a mixture of pure potassium carbonate and sugar charcoal heated, in a porcelain tube, he observed that carbon monoxide was evolved at first in much greater volume than that of the nitrogen passed in. When the evolution of carbon monoxide ceased he found in two experi-

[1] The bracketed figures are Thompson's; they are recalculated on the assumption that Troy weight was used.

ments at a 'full red heat' that 11¼ and 12⅔ p.c. of the potash had been converted into cyanide, whereas at 'whiteness, much above the melting-point of copper,' the production of cyanide appeared much greater.

The repetition of Fownes' experiment by several chemists added little to our knowledge, and may be dismissed in a few words. Erdmann and Marchand (J. pr. Chem. 1842, 26, 407) observed only a doubtful trace of cyanide; Liebig and Wöhler (Handwörterbuch der Chemie, 1842, ii. 384) could not confirm Fownes' result; and Delbruck (J. pr. Chem. 1847, 41, 161) also obtained a mere trace of cyanide. None of these authors gives details of their methods. Bunsen and Playfair (Brit. Ass. Rep. 1845, 142), on the other hand, by heating a mixture of pure potassium carbonate and sugar charcoal in a gun barrel in a current of nitrogen at a temperature high enough to form potassium (about 1200°), obtained 6·982 grams of silver cyanide from an unmentioned quantity of potash. It may be surmised that the different results noted were due to differences of temperature.

In addition to these laboratory experiments, a most remarkable attempt was made to develop this process on a manufacturing scale. Possoz and Boissière (Eng. Pat. 9985 of 1843, granted to their agent A. V. Newton) began their experiments at Grenelle, near Paris, in 1843, but transferred the plant in 1844 to the works of Messrs. Bramwell & Co. (one of the leading prussiate makers of that time) at Newcastle-on-Tyne. The experiments were carried on by Mr. Bramwell and Mr. F. R. Hughes until 1847, and a detailed account of them, furnished by Mr. Hughes, was published by Graham (Report of Juries, Exhib. of 1851, 1, 95).

Wood charcoal was soaked in a solution of ordinary potash and dried, yielding a mixture containing about 20 p.c. K₂O. This was, at first, heated in vertical fire-clay retorts of small diameter, which were fired externally. Owing to the low thermal conductivity of the retorts and of the charcoal, the heat penetrated the mass very slowly, and the output of a tube was small. It may be pointed out that this very serious difficulty is accentuated by the endothermic nature of the reaction, which was unknown at that time; it is not only necessary to heat the charge to the reaction temperature, but the large quantity of heat absorbed by the reaction

$$K_2CO_3 + 4C + N_2 = 2KCN + 3CO - 129 \text{ Cals.}$$

must also be supplied.

After a number of alterations, retorts were adopted, which were built of ordinary firebrick; they were 2 feet in internal diameter, and were heated for a length of 6 to 8 feet to a temperature sufficient to produce cyanide. In an upper prolongation, the wet charcoal was dried and preheated, and in a lower, unheated extension, made of cast iron, the product was cooled down, and then discharged, by means of an arrangement which permitted a periodical withdrawal of a part of the charge, into a solution of a ferrous salt, into which the lower end of the cast-iron tube dipped. A ring of small slots was left in the brick retort at every third or fourth course of bricks, through which the hot

mixture of nitrogen and carbon dioxide in the furnace was drawn into the retort by means of an aspirator attached to the upper end. In this way the difficulty of heating the charge to its centre was overcome. The highest temperature in the furnace was sufficient to soften a Stourbridge fireclay brick throughout its substance (1350°-1400° ?). The hot gases were aspirated upwards, drying and preheating the fresh charge in the upper part of the retort. As much as one-half of the alkali in the cyanised charcoal produced was found to be in the form of cyanide, and 7 or 8 retorts of the dimensions given yielded 36–40 cwts. of prussiate of potash per week, under favourable circumstances. About one-half of the charcoal used was consumed, and 3 parts of potash were used for 1 part of prussiate made. About one-third of the potash was accounted for by the prussiate; one-third remained in the refuse charcoal, which could not be profitably lixiviated; and the remainder combined with the bricks of the retort, or was volatilised up the chimney. The financial failure of the process was due to the losses of potash and to the short life of the retorts.

R. Hoffmann (Report of Juries, Exhib. of 1862, 59) also tried large-scale experiments at Oedenwald in the Black Forest, in 1858–1859, which may be referred to as a further illustration of the difficulties mentioned above. The alkalised coke was heated in wrought-iron tubes, not more than 1 foot in diameter, protected with fireclay. The furnace was heated to a bright, white heat, which fused the common brick work behind the firebrick lining, but only minute quantities of cyanide were formed; the failure is ascribed to too low temperature, for it was found that the middle portion of the coke in a tube was far from being white hot.

In 1878, C. A. Fawsitt (Eng. Pat. 4544 of 1878) described a method of making ammonia by this process. In his experiments, which were made at St. Rollox, Glasgow, he used sodium carbonate instead of potash (J. Soc. Chem. Ind. 1890, 9, 30). Using 3-inch or 4-inch wrought-iron tubes, he obtained as much as 50 p.c. of the theoretical yield of ammonia, but with 6-inch cast-iron tubes the yield was much smaller, because the cast iron would not withstand the temperature needed. These experiments, therefore, indicate that a temperature exceeding 1100° (the approximate melting-point of cast iron) is required; although, in this case, the differences may have been due, in part, to the facts that a tube of larger diameter would give worse results even with the same external temperature, and that the nitrogen used with the 6-inch tubes contained from 3 to 5 p.c. of oxygen.

The patents of Victor Alder of Vienna are of interest, because they contain a clear recognition of the catalytic rôle of iron, and of the necessity of obtaining intimate admixture of the reacting constituents, together with sufficient porosity to admit of free access of nitrogen. Alder proposed to heat an intimate mixture of alkaline material and carbon in a closed vessel, in an atmosphere of nitrogen, and said: 'The addition of finely divided iron greatly promotes the conversion into cyanide, but is not absolutely essential to the success of the operation' (Eng. Pat. 1004 of 1880). In Eng. Pat. 5617 of

1881 he states that the reaction only succeeds in presence of carbonising gases, such as hydrocarbons or carbon monoxide, and that metals 'capable of fixing and transmitting the carbon, such as iron, chromium, manganese, nickel, or cobalt, greatly promote the conversion.' The charge is prepared, for example, by mixing a solution of the alkali with charcoal and adding sawdust or other substance, which, when heated, will yield a porous mass; or a thin paste of the alkaline solution and finely ground charcoal containing some binding material is spread out on the surface of lumps of charcoal. The 'carbonising metal' is to be added as such, as oxide or in the form of a solution of a salt which, when heated in a current of steam, will decompose, leaving a deposit of the oxide, which, in the cyanising process, will be reduced to metal. Alder appears, however, to have been under the impression that the success of a technical process depends on the employment of the cheapest raw materials, however unsuitable they may be, and a great part of the specifications consists of descriptions of the preparation of alkali-carbon mixtures from such substances as alkali sulphates, limestone, and coal, as in the Le Blanc alkali process; the failure of the process is not, therefore, surprising.

The catalytic action of iron was re-discovered by E. Tauber in 1899 (Ber. 1899, 32, 3150; and more fully in Die Chem. Ind. 1903, 26, 26). Trials of different kinds of carbon and different alkalis showed that potash or soda and wood charcoal are the most active materials. An intimate mixture of alkali and charcoal was made by soaking sawdust in the alkaline solution and carbonising the mixture; iron (reduced by hydrogen) in fine powder was added to this, 3 parts of iron to 1 part of soda giving the best results. The mixtures were heated, in iron boats enclosed in glass tubes, for 1¼ hours at temperatures between 'dark and moderate' red heats, a current of purified nitrogen being passed. In some cases more than 25 p.c. of the soda used was cyanised, but usually a conversion of 10 p.c. was not exceeded. Magnesium, tungsten, chromium, and nickel were found to possess some catalytic activity, though much less than iron.

Between 1843 and 1912 some 30 patents were granted in Great Britain for modifications of the process described by Possoz and Boissière, in which the blast furnace type of apparatus recurs frequently; no details of the results obtained, or of the causes of failure, appear to have been published. Since 1912 the numerous patents of J. E. Bucher (especially Eng. Pats. 27713 of 1912; 23292 and 13332 of 1914; 2286 of 1915), which are being developed by the Nitrogen Products Co. of Providence, Rhode Island, at their works at Saltville and Niagara Falls, have directed renewed attention to the catalytic action of iron. Prof. Bucher's results (J. Ind. Eng. Chem. 1917, 9, 233) surpass any which have previously appeared in print; this appears to be due partly to the fact that he has clearly realised that the necessary conditions, already known separately, must be fulfilled simultaneously, and partly to the ingenuity and care devoted to the detailed adaptation of means to this end.

Carbon and iron oxide are separately ground

in a ball mill to pass 100-mesh sieve, and then re-ground together, after which dry sodium carbonate is added. The open-grained structure which is necessary to allow nitrogen to pass through the material is obtained by briquetting. This is done by kneading the powder, at about 100°, with a little more water than is required to form the monohydrate Na_2CO_3,H_2O, and squirting the paste into small rods about 1 inch long and $\frac{1}{4}$ inch diameter. These are dried at once, before cooling, because the expansion due to the formation of the decahydrate at temperatures below 35° causes them to fall to powder. When heated above the melting-point of sodium carbonate (852°) these little briquettes become plastic to some extent, but retain their shape sufficiently well to permit free circulation of gases through a column several feet thick. Mixtures of coke, iron, and sodium carbonate in proportions from 2 : 2 : 1 to 2 : 2 : 2 give satisfactory results, the smaller proportion of sodium carbonate giving the fastest reaction owing to the greater accessibility of the active carbon-iron surfaces to nitrogen. The reaction is said to begin about 700°, and the eutectic temperature of iron-carbon (about 1150°) should not be exceeded because fusion of the particles of iron into larger globules diminishes their active surface. The speed of the reaction, under suitable conditions, is considerable; for example, the 2 : 2 : 1 mixture heated, in 13 minutes, from 710 to 920 in a current of nitrogen, yielded a product containing 15·2 p.c. NaCN, 92 p.c. of the sodium being in the form of cyanide. Sodium cyanide volatilises somewhat freely at 900°–950°, so that in a stationary column of material in a vertical tube, the upper layers are much richer than the lower ones, and a considerable loss of alkali is observed ; it is anticipated that this will not occur in a continuous process, since the incoming fresh charge will condense the cyanide vapour.

In order to supply the necessary quantity of heat $(Na_2CO_3+4C+N_2=2NaCN+3CO-138·5$ Cals.) at a sufficient rate, Bucher proposes, for example, to use the hot charge itself as an electrical resistance (cf. Readman's apparatus, below), or to use electrically heated molten iron saturated with carbon and to pass a mixture of nitrogen and sodium vapour through it.

Producer gas may be used at high temperatures, but the cyanide disappears if the product is allowed to cool in an atmosphere containing carbon monoxide. This may be due to the formation of carbon dioxide, as Bucher suggests, by the reaction $2CO=CO_2+C$, which is accelerated by iron; it is also possible that the reaction $Na_2CO_3+4C+N_2=2NaCN+3CO$ is reversible, as has been proved in the analogous case of barium carbonate.

Since this was written the reversibility of the reaction has been proved by J. B. Ferguson and P. D. V. Manning (J. Ind. Eng. Chem. 1919, 11, 946). Mixtures of sodium cyanide or of sodium carbonate (3 parts), charcoal (1 part), and iron (1 part) were heated in presence of definite mixtures of carbon monoxide and nitrogen. The composition of the product was not affected by the nature of the initial materials, but varied with the temperature and the composition of the gas. With 5 p.c. CO, for example, 75 p.c. of the alkali was cyanised at

946° and 80 p.c. at 1000°; with 48 p.c. CO, 27·5 p.c. and 59 p.c. were cyanised at the same temperatures. Owing to volatilisation of cyanide it is probable that true equilibrium was not realised ; the error will be greatest for products rich in cyanide.

C. O. Brown (J. Ind. Eng. Chem. 1919, 11, 1010) has described the plant which was erected by the Government of the United States in 1917–18 to produce 10 tons of sodium cyanide daily by the Bucher process. Briquettes, made in the way described above, were heated at 1000° in vertical, gas-fired, steel, or nichrome tubes in a current of very pure nitrogen. The product, containing about 20 p.c. NaCN, was extracted with liquid, anhydrous ammonia ; by this means the formation of ferrocyanide is avoided, and any unchanged alkali is left undissolved in the residues which are reground with sufficient carbon and soda and reused. Evaporation of the ammonia solutions leaves sodium cyanide, containing 92 p.c. NaCN, as a white powder. The loss of ammonia was about 2 lbs. per 100 lbs. cyanide made. Each steel tube produced about 7½ lbs. of sodium cyanide hourly, and had a life of 11–14 days. The work was abandoned after the armistice in 1918.

It may be mentioned here that the Cassel Cyanide Co., of Glasgow, has used iron as a catalyst in the manufacture of cyanides from atmospheric nitrogen since the year 1909, when the writer first became fully aware of its great activity under suitable circumstances. The work in which sodium carbonate was employed as raw material was carried out entirely by Mr. J. H. Young. Setting out from finely divided, precipitated ferric oxide and charcoal (the purest and most active form of carbon available), the mixtures were made by grinding these substances separately and then together, finally adding the dry sodium carbonate and re-grinding. The necessary porosity of the material to be treated with nitrogen was secured by adding a quantity of the very bulky charcoal obtained by carbonising shavings ; the addition of 15 parts of this material to a ground mixture of 20 parts of sodium carbonate, 8 parts ferric oxide, and 15 parts charcoal, gave good results, 60–80 p.c. of the alkali being cyanised at 900°. The residual charcoal-iron mixture resulting from the lixiviation of the cyanised mass gave even better results than a fresh mixture. A larger scale, continuous plant was at work in 1913, in which the mixtures were heated in vertical steel tubes, of 6 inches bore and about 10 feet long, of which a length of about 5 feet was heated to the working temperature. The lower part of the tube served for cooling the product, which was withdrawn by means of a horizontal spiral conveyor, fresh material being fed in at the top of the tube. Pure nitrogen was employed, and very careful measurements of the temperature showed that under satisfactory working conditions the temperature in the axis of the tube was 900°, near the inside wall of the tube it was 950°, whilst a thermocouple in the furnace in contact with the outer wall of the tube indicated 1010°. These measurements indicate quite clearly the necessity of using tubes of small diameter when external heating is relied on. Temperatures higher than those mentioned were found to be undesirable

owing to their serious effect on the life of the steel tubes, and also on account of the danger of fusing part of the iron catalyst, and so diminishing its active surface. Each tube of the dimensions mentioned produced from 40 to 50 lbs. of sodium cyanide in 24 hours, the product containing from 21 to 26 p.c. NaCN.

The results described, together with the older experience of the reaction between alkalis and nitrogenous organic matter, make it easy to understand the occurrence of cyanides in kelp, barilla, Le Blanc alkali, and the residues from the preparation of potassium (which were known to Lewis Thompson in 1839), and especially in the blast furnace. Clark (Phil. Mag. 1837, 10, 729) described the occurrence of cyanide at the Clyde Iron Works, in a furnace using raw coal and hot blast, in quantities such that wheelbarrows full could be obtained. Zincken and Bromeis (J. pr. Chem. 1842, 25, 246) found a quantity of potassium cyanide in the charcoal remaining in the hearth of a furnace in the Harz which had been closed down. This furnace had been worked with charcoal and a hot blast. Redtenbacher (Annalen, 1843, 47, 150) described the formation of potassium cyanide in quantity (it was used for electroplating) in a charcoal iron furnace at Mariazell in Steiermark, which was also worked with blast heated as high as 350°. Bunsen and Playfair (Brit. Ass. Rep. 1845, 142) observed the production of more than 2 cwts. per day of potassium cyanide in the coal-fired furnace at Alfreton, which worked with blast at 330°; they also showed that the potassium was derived mainly from the iron ore used, the furnace charge containing sufficient potassium to produce 377 lbs. of KCN per day. The cyanide was found in the hottest part of the furnace, 2 feet 9 inches above the tuyeres, but some 7 feet higher there was very little. Sir Lowthian Bell (J. Soc. Chem. Ind. 1890, 9, 710) gives the following figures for the distribution of cyanogen in a more modern furnace at the Clarence Works, which was worked with coke and Cleveland iron ore and blast at about 700° :—

Height above hearth	8 ft.	24 ft.	52½ ft.	60 ft.	escape pipe
Grams CN per cb. m. gas	49·06	15·76	7·67	5·94	4·73

It is generally assumed, probably correctly, that the blast furnace cyanide is produced from free nitrogen, but it is interesting to note that Sir L. Bell's furnace consumed 50 tons of coke per day, which probably contained at least ⅓ ton of combined nitrogen.

The mechanism of the reaction which occurs between carbon, alkali carbonates, and nitrogen, and the rôle of iron, are still quite obscure. The old view, that carbon and nitrogen ('nascent' or otherwise) unite to form cyanogen which is then fixed by alkalis, is extremely improbable in view of the nature of the equilibrium

$$2C + N_2 \rightleftarrows C_2N_2$$
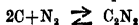
(v. Cyanogen), and of the fact that no one has succeeded in isolating a trace of cyanogen gas made by the direct union of the elements. The possibility that a carbide may be an intermediate product is discussed later. It is, at least, an ascertained fact that some metallic acetylides do combine with nitrogen, although the behaviour of

the alkali metal derivatives has hardly been investigated. The intermediate formation of free alkali metal has also been asserted to be necessary, but as the alkali metals (except lithium) do not combine directly with nitrogen, whereas they do combine with carbon, this seems to be identical with the assumption of the intermediacy of a carbide. No valid experimental evidence appears to have been advanced in support of the existence of any intermediate compound.

1b. Action of Nitrogen on Alkali Metals and Carbon.

This reaction appears to have been observed for the first time by R. F. Marchand (J. pr. Chem. 1850, 49, 351). A statement that cast iron and steel contain from 0·5 to 1·2 p.c. of nitrogen induced him to test some 30 samples of cast iron by Lassaigne's method, that is, by heating the sample to redness, in a test tube, with potassium, extracting the product with water, and applying the Prussian blue test to the solution. A copious precipitate was obtained in every case. He found, however, that, when the residue of iron was dried and again heated with potassium, there was a further production of Prussian blue, and that this continued so long that, with 8 grams of powdered iron, it was impossible to exhaust the reaction. This led Marchand to suspect that the nitrogen was derived from the air, and he proved that this was the case by carrying out the reaction in an atmosphere of hydrogen or of carbon dioxide, when no more than a doubtful trace of blue was obtained, and, further, by heating the mixture of cast iron and potassium (after drying it in a current of hydrogen) in an atmosphere of nitrogen in a closed tube, when he found that the nitrogen was completely absorbed. He also showed that steel behaves like cast iron, but soft iron does not. Marchand did not obtain the reaction with a mixture of carbon and iron obtained by heating ferric succinate or benzoate, and therefore concluded that success depends on the carbon being in chemical combination with the iron.

The success of Lassaigne's test, when applied to organic substances containing sulphur, had been questioned by O. Jacobsen, who recommended the addition of reduced iron in such cases. Making the test in this way, I. Remsen (Amer. Chem. J. 1881, 3, 134) obtained Prussian blue from substances, such as pure cane sugar and sodium potassium tartrate, which contain no nitrogen. After proving that the reduced iron employed was not the source of the nitrogen, Remsen heated a mixture of the tartrate, pure reduced iron and sodium, first in hydrogen to dry it, and then in nitrogen, obtaining a very large precipitate of Prussian blue. He also made the new observation that the iron powder loses its activity when it is superficially oxidised by exposure to air, which may perhaps explain Marchand's failure to obtain the reaction with his mixtures of iron and carbon.

The reaction was re-discovered by E. Täuber (Ber. 1899, 32, 3150), whose experience coincided almost exactly with that of Remsen.

H. Y. Castner, in 1894, patented a process in which sodium was allowed to flow downwards over a column of red-hot charcoal in

an iron vessel, a current of nitrogen passing upwards through it (Eng. Pat. 12218 of 1894). It is doubtful whether this process received more than a cursory trial. It was taken up again by the Roessler and Hasslacher company about 1910. They find that a mixture of sodium vapour and nitrogen reacts with charcoal in the absence of iron at 650°, and that the speed of reaction is sufficient for manufacturing purposes at temperatures above about 800°. (H. Philipp, Chem. and Met. Eng. 1920, 22, 313; U.S. Pats. 1249821, 1917; 1235887, 1917).

In 1912, J. E. Bucher applied for a patent for the manufacture of cyanide by the direct union of its elements in presence of iron (Eng. Pat. 11797 of 1913; U.S. Pats. 1082845 of 1913; and 1116559 of 1914). A temperature of from 500° to 800° is said to be suitable, and iron and carbon are to be intimately mixed. Like Marchand, Bucher also observed the removal of carbon from cast iron or steel by the action of sodium and nitrogen on them. He also follows Marchand in adopting the view that iron acts as a solvent of carbon, the dissolved carbon being supposed to be capable of entering into combination with sodium and nitrogen. When sodium carbonate is used, it is assumed that a little metallic sodium is formed by the action of carbon, even at the low temperature (700°) at which the reaction proceeds, the removal of this, by conversion into cyanide, disturbs the equilibrium and permits the decomposition of further quantities of sodium carbonate. This hypothesis appears to be open to the criticism that it makes the extremely rapid rate of formation of cyanide depend on the rate of solution of solid carbon in solid iron; it also fails to make clear why the usually inert nitrogen becomes so active.

The Cassel Cyanide Co.'s experiments with this process were begun, as already stated, in 1909; in 1911 engineering difficulties had been so far surmounted that a unit plant producing about 50 lbs. of cyanide hourly was at work. From the experience thus gained a larger industrial unit was designed and erected, which was producing cyanide for some time before war was declared in 1914.

1c. *Action of Nitrogen on Barium Carbonate and Carbon.*

In 1860 Margueritte and De Sourdeval (Eng. Pat. 1171, of 1860; Compt. rend. 1860, 50, 1100) discovered that a mixture of barium oxide and carbon absorbs nitrogen readily forming barium cyanide. Ludwig Mond (Eng. Pat. 433 of 1882; J. Soc. Chem. Ind. 1889, 8, 505) experimented with this process in 1882. He found that a temperature of 1200° was required for the formation of cyanide, and that the reaction goes best about 1400°. The barium compounds fuse readily at these temperatures and attack the fireclay retorts. To avoid this he briquetted them with an excess of carbon and pitch. The apparatus used was similar to that of Possoz and Boissière, and 40 p.c. of the barium used was readily cyanised. The object of Mond's experiments was the production of ammonia, and he abandoned this process in favour of the more promising method of acting on coal with air and steam in large excess (*see* AMMONIA).

As Mond pointed out, the reaction is endothermic

$$BaCO_3 + C = BaO + 2CO - 101.2 \text{ Cals.}$$
$$BaO + 3C + N_2 = Ba(CN)_2 + CO - 43.1 \text{ Cals.}$$
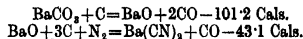
The introduction of internal electrical heating by Readman (Eng. Pat. 6621 of 1894) therefore marks a very considerable step in advance. His process was worked by the Scottish Cyanides Co. at Leven in Fifeshire, between the years 1899 and 1907. Considerable quantities of sodium cyanide of excellent quality were produced, but the financial results were unfavourable. The following account of the process in its final form is believed to be substantially accurate.

Barium carbonate, produced in a later stage of the process, was intimately mixed with ground coal to a thick paste, which was dried and coked in ordinary gas retorts. The granular mixture of barium oxide and coke so produced was then fed into an electric furnace, consisting of a vertical shaft of circular cross-section, lined with magnesia bricks. A ring of carbon blocks in the wall of the shaft near its lower end formed one electrode, a carbon cylinder suspended in the mouth of the shaft formed the other. The alternating current passed between these electrodes through the granular mass of coke and barium oxide, heating it to a high temperature. A current of producer gas with about 70 p.c. of nitrogen, passed upwards through the mass, which was constantly fed downwards into a cooling chamber by means of a plate and rotating arm which closed the lower end of the shaft, fresh material being fed in to the annular space round the upper electrode. The cooled product was lixiviated with water, and the resulting solution, containing barium cyanide, cyanamide, and hydroxide, treated with barium bicarbonate. After filtering off the barium carbonate, the solution of sodium cyanide was concentrated *in vacuo* and then passed over cooling coils depositing crystals of the hydrate NaCN,2H₂O. These were separated from the mother liquor in a centrifugal machine, and then dehydrated by heat and the powder briquetted. The mother liquor, from which no further crystals could be obtained, was distilled with sulphuric acid to recover the residue of hydrocyanic acid.

The chemistry of this process has been studied in some detail at temperatures up to 1150°, but little is known of it at higher temperatures. Undecomposed barium carbonate, as Finkelstein (Ber. 1906, 39, 1585) showed, does not melt at 1350°, but when heated alone or with carbon, it is partially converted into barium oxide, which yields readily fusible mixtures with the carbonate. Le Chatelier, for example, found that pure decomposed barium carbonate melts at 795°. The fusibility of the mixtures is increased by the formation of barium cyanide (which melts about 600°), so that the material under treatment in this process is a liquid phase of variable composition.

Kühling and Berkhold (Ber. 1908, 41, 28) found that when a mixture of barium carbonate and carbon is heated in a current of nitrogen under constant conditions, a little more than 40 p.c. of the barium combines with nitrogen at 1150°, and that at lower temperatures the quantity combined diminishes, reaching zero at about 925°.

Ewan and Napier (J. Soc. Chem. Ind. 1913, 32, 467) also found that the absorption of nitrogen begins at 925°. They showed, however, that it depends on the two reversible reactions $BaCO_3 + C \rightleftharpoons BaO + 2CO$ and

$$BaO + 3C + N_2 \rightleftarrows Ba(CN)_2 + CO$$
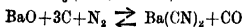
If carbon monoxide is allowed to accumulate, therefore, the change is brought to a standstill, if it is swept out with large quantities of pure nitrogen a considerable portion of the barium may be cyanised even at comparatively low temperatures. Using 29 molecules of nitrogen to each molecule of BaO, for example, over 40 p.c. of the barium combined with nitrogen in 2 hours at 960°.

The pressure of carbon monoxide in equilibrium with pure barium carbonate and carbon is relatively large, it falls, however, to very low values for the dilute solutions of the carbonate in barium oxide or cyanide. For this reason the greater part of the barium carbonate decomposes before any cyanide is formed, but the decomposition is never complete.

When a mixture of $BaCO_3 + BaO + C$ or of $Ba(CN)_2 + BaCN_2 + C$ is heated in a mixture of carbon monoxide and nitrogen of definite composition until no further change occurs, the percentage of the barium in the product, which is combined with nitrogen (as cyanide or cyanamide), is independent of the composition of the initial mixture, and depends only on the temperature and on the composition of the gas used. The maximum quantities of barium which can combine with nitrogen under different conditions, observed in this way, are given in the following table :—

P.c. of CO in the gas	P.c. of the barium combined with nitrogen		
	1000°	1100°	1150°
0	50	50	50
10	28	41	44
20	5	32	38
30	—	22	32
40	—	13	26
50	—	4	15
70	—	—	9

The curves drawn through the experimental points appear to be straight lines converging towards 50 p.c. conversion for pure nitrogen ; it is probable, however, that this is not their true form at very small concentrations of carbon monoxide, because a product in which 57·1 p.c. of the barium had combined with nitrogen was obtained by continuing the heating for 82 hours at 1100° with nitrogen containing only 0·1 p.c. of CO. For practical purposes, the rapid increase in the quantity of carbon monoxide required to reverse the reaction at higher temperatures is important.

In addition to the two equilibria just mentioned, the reaction $Ba(CN)_2 = BaCN_2 + C$ occurs. Pure barium cyanide decomposes even at 500°, the reaction is a slow one, which is accelerated by iron. The results appear to show that at temperatures between 600° and 1000°, and in absence of barium oxide, the decomposition ceases when about two-thirds of the

nitrogen is in the cyanamide form ; in presence of barium oxide the change does not go so far. The relative quantities of cyanide and cyanamide produced by the action of nitrogen on mixtures of barium oxide and carbon are very erratic, anything from 0 to 70 p.c. of the nitrogen fixed may be in the cyanamide form, the average of 36 experiments was 15 p.c.

The equilibrium pressure of carbon monoxide in the reaction $BaO + 3C \rightleftarrows BaC_2 + CO$ was found to be 1 mm. of mercury at 1200°. Cyanide formation therefore proceeds freely in presence of quantities of carbon monoxide, which are quite incompatible with the existence of barium carbide. The suggestion that barium carbide is an intermediary in this process is, therefore, incorrect.

The effect of pressure was studied by Hempel (Ber 1890, 23, 3388). The mixture of barium oxide and carbon was heated for 15 minutes by the same quantity of electrical energy in a closed bomb ; the quantity of hydrocyanic acid obtained increased 16 times when the nitrogen pressure was increased from 1 to 60 atmospheres. The improvement may have been due to greater reaction velocity of the more concentrated nitrogen or to a larger value of the ratio of nitrogen to carbon monoxide in the bomb. Stahler (Ber. 1916, 49, 2292), by a somewhat similar method, finds that with 60 atmospheres N pressure a product containing 74 p.c. of barium cyanide and no appreciable quantity of cyanamide is obtained.

The addition of barium chloride or of potassium carbonate to the mixture of barium oxide and carbon neither reduces the minimum temperature nor increases the speed of the reaction.

The effect of the addition of calcium and barium fluorides was studied by N. Caro (Zeitsch. angew. Chem. 1910, 3, 2405) at temperatures about 1100° and 1200°. Since the quantity of carbon monoxide in the nitrogen was not observed it is impossible to draw definite conclusions from the results ; it is, however, of interest that in the 15 experiments recorded the quantity of the barium which combined with nitrogen never exceeded one-half of that present.

Very little information exists about the course of the reaction at higher temperatures. From Eng. Pats. 2133 of 1907, and 22039 of 1906 (Badische Co.), it may be gathered that 80 p.c. of the barium can be combined with nitrogen at 1500° ; and, according to Kaiser (Fr. Pats. 454237–8 of 1913), 90–95 p.c. of the theoretical quantity of nitrogen is absorbed, when barium carbonate and carbon are heated at ' 900° to 1400° ' in nitrogen and cooled in it under pressure. It appears, therefore, that the inactivity of one-half of the barium, which has been shown to exist at temperatures below 1200°, may disappear at considerably higher temperatures ; possibly because a different mechanism comes into play. Ewan and Napier (l.c.), by applying Nernst's thermodynamic theorem to their measurement of the equilibrium pressure (p_{CO} in mm. of mercury) of the reaction $BaO + 3C \rightleftarrows BaC_2 + CO$, showed that, at absolute temperature T

$$\log_{10} p_{CO} = -\frac{16250}{T} + 1·75 \log_{10} T + 5·48$$

from which the value of $p_{00}=100$ mm. at 1500° and 1026 mm. at 1700°. M. Kahn (Compt. rend. 1907, 144, 913) found that barium carbide is formed from barium oxide and carbon heated in a well-closed crucible at the melting point of platinum (1760°); the equilibrium pressure at 1760° is, therefore, greater than 1 atmosphere, in approximate agreement with the calculated value. It is therefore possible that barium carbide is an intermediate product at high temperatures.

2a. Action of Nitrogen on the Carbides of Metals.

F. R. Hughes (Report of Juries, Exhib. of 1851, 1, 95) suggested that the first stage of the reaction between potassium carbonate and carbon might lead to the formation of potassium carbide, and that this might combine directly with nitrogen. Potassium carbide is actually formed in this way, E. Davy (Brit. Ass. Report, 1836, ii. 62), having discovered acetylene by treating with water, the black product of an unsuccessful attempt to prepare potassium. Berthelot (Compt. rend. 1868, 67, 1141) was led to suggest the same mechanism by the analogy with his synthesis of hydrocyanic acid from acetylene and nitrogen. He also showed that the products of the action of potassium on potassium carbonate or on carbon monoxide contain potassium acetylide. The action of nitrogen on the alkali metal carbides has not been investigated in detail. Frank and Caro (Eng. Pat. 15066 of 1895) mention that they combine at a 'dark red heat' forming cyanides.

The absorption of nitrogen by the carbides of calcium, strontium, and barium has been much more completely studied. Moissan (Compt. rend. 1894, 118, 503, and 684) found that pure, dry nitrogen did not react with the pure carbides even at 1200°, although the product obtained from barium carbide yielded a little ammonia when boiled with water. In 1895 Frank and Caro (Eng. Pat. 15066 of 1895), and T. L. Willson (Eng. Pat. 21997 of 1895), discovered independently that the impure carbides absorb nitrogen. According to Frank and Caro, moist nitrogen is necessary when the pure carbides are used, but not with impure substances; they also found that barium carbide yields the corresponding cyanide, but obtained an 'unsatisfactory result' with calcium carbide unless it was mixed with barium or sodium carbide. Willson proposed to treat the carbides with nitrogen either during their formation in the electric furnace, or subsequently in a separate operation. He also appears to have found difficulty with calcium carbide, and says that a cyanide or some more complicated nitrogen compound is formed. The fact that a large part of the combined nitrogen is in the form of a cyanamide salt was discovered by F. Rothe, working under Frank's direction, in 1898 (Zeitsch. angew. Chem. 1903, 658), and was published in Frank and Caro's Eng. Pat. 25476 of 1898.

Frank and Caro at first attempted to apply their discovery to the manufacture of cyanides.

Finely ground barium carbide, made in the electric furnace, was heated at about 700° in presence of pure nitrogen. The product contained about 11 p.c. of nitrogen, 30 p.c. of which was in the form of barium cyanide, the remainder being barium cyanamide. In order to convert the cyanamide into cyanide, the material was heated with dry sodium carbonate and carbon. The sodium carbonate may convert the barium cyanamide into the sodium salt, which then takes up carbon in the way discovered by Dreschel,

$$BaCN_2 + Na_2CO_3 = Na_2CN_2 + BaCO_3$$
$$\text{and } Na_2CN_2 + C = 2NaCN$$
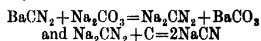
By extracting the product with water, converting the sodium cyanide into ferrocyanide, and then fusing it with sodium, about 86 p.c. of the nitrogen fixed was obtained in the form of marketable sodium cyanide (G. Erlwein, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 646). The process, however, even in this form, did not pay, and the cheaper calcium carbide was therefore tried. Commercial calcium carbide absorbs nitrogen at about 1100°, yielding a product containing from 20 to 23·5 p.c. of nitrogen, which is wholly in the form of calcium cyanamide $CaC_2 + N_2 = CaCN_2 + C$. Details of the manufacture of calcium cyanamide are given in the article on NITROGEN, ATMOSPHERIC, UTILISATION OF. By heating this product with sodium chloride, from 90 to 95 p.c. of the cyanamide is said to be converted into sodium cyanide. (G. Erlwein, loc. cit., G. Erlwein and Frank, U.S. Pat. 708333, 1902.)

It is not easy to obtain such a high yield in the laboratory; Kitawaki and Kusano, for example (J. Chem. Ind. Tokyo, 1917, 20, 234), state that when 10 parts of calcium cyanamide (18·6 p.c. N) are heated with 16 to 24 parts of salt, and 2 parts of charcoal for 10 minutes at 900°–950°, and the fused product cooled in absence of oxygen, it contains more than 70 p.c. of the theoretical quantity of cyanide.

Large-scale experiments were carried on in Germany with but little success; a description of these, up to 1914, has been published by W. S. Landis (Chem. Met. Eng. 1920, 22, 265). In the latest modification, from 2 to 3 parts of salt were fused separately, and 1 part of calcium cyanamide added gradually in order to control frothing. The highest temperature used was 960°, and from 40 to 75 p.c. of the nitrogen was obtained in the form of cyanide.

In 1916 the process was installed at Niagara. It was soon found that the troublesome evolution of gas was almost suppressed by the addition of a little calcium carbide, and that much better results were obtained by raising the temperature to 1200°–1400° (H. P. Eastman, U.S. Pat. 1282395, 1918), and also that the cyanide disappears when the fused product is allowed to cool slowly, the reversion apparently occurring between 400° and 700° (H. Freeman, U.S. Pat. 1282405, 1918). In 1919 the process was, therefore, carried out by feeding a mixture of calcium cyanamide (1 part), salt (about 0·8 part), and calcium carbide (0·05 to 0·1 part) into a single phase electric furnace of the arc-resistance type with conducting hearth and a single suspended electrode. The furnace treats about 30 tons daily. The mixture fuses, and is run off almost continuously into a pan in which a water-cooled drum rotates, taking up a thin layer of the fused material which solidifies and is scraped off in thin flakes which contain cyanide (possibly the calcium salt) equivalent to 36 p.c. NaCN. The

efficiency on the nitrogen is about 90 p.c. The equivalent of 975 tons of sodium cyanide was made in 1917, 1050 tons in 1918, and 1250 tons in 1919. The chemistry of this process is still incompletely known; Landis states that cyanide is formed even when little or no salt is used, which suggests that the principal change is represented by the reversible reaction

$$CaCN_2 + C \rightleftharpoons Ca(CN)_2$$
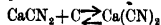
The initial frothing may be due to the decomposition of sodium cyanamide

$$2NaCN_2 = 2NaCN + N_2 + 2Na$$
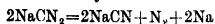
the graphitic carbon present not being sufficiently active at lower temperatures to convert it quickly into cyanide; the addition of calcium carbide is supposed to supply the necessary active carbon.

2b. Action of nitrogen on acetylene.

In 1863 Berthelot had shown (Ann. Chim Phys 1863, [3] 67, 52) that acetylene is formed in the electric arc between carbon electrodes in an atmosphere of hydrogen, and also that hydrocarbons in general yield acetylene when induction spark pass through their vapours. The careful measurements of Bone and Jordan (Chem. Soc. Trans. 1901, 1042) indicate that, when equilibrium is established in the gas surrounding a carbon arc burning in hydrogen or hydrocarbon vapour, it contains 90–91 p c H_2, 7–8 p.c. C_2H_2, 1·25 p.c. CH_4 and 0·75 p.c. C_2H_6, no other hydrocarbons being present.

In 1868 Berthelot(Compt rend.1868,67,1141) discovered that acetylene and nitrogen combine, under the influence of strong induction sparks, to form hydrocyanic acid, and that the reaction $C_2H_2 + N_2 \rightleftharpoons 2HCN$ is reversible. Taken together with his earlier observations on the formation of acetylene, this led him to the generalisation that hydrocyanic acid must be formed in the carbon arc burning in mixtures of hydrogen and nitrogen or when sparks are passed through mixtures of nitrogen and hydrocarbons. The cyanogen compound observed when the arc burns between carbon electrodes in an atmosphere of nitrogen is hydrocyanic acid, the hydrogen of which is derived from the electrodes or from water vapour. A mixture of 10 vols. C_2H_2, 14·5 vols. N_2, and 75·5 vols. H_2 is suitable for the synthesis of hydrocyanic acid, since mixtures richer in acetylene deposit carbon. Dewar (Proc. Roy. Soc. 1879, 29, 188, and 1880, 30, 85) confirmed Berthelot's observations on the formation of hydrocyanic acid in the arc, and also showed that it is formed when a mixture of hydrogen and nitrogen is passed through a carbon tube heated externally by an electric arc. The minute traces of hydrocyanic acid found in the slightly luminous flame of a Bunsen burner (Lüdeking, Annalen, 1888, 247, 122) are doubtless due to this reaction.

Subsequent investigations add little to the information given by Berthelot; Hoyermann (Chem. Zeit. 1902, 26, 70) passed a mixture of nitrogen (2 vols.) and acetylene (1 vol.) into the arc through tubular carbon electrodes and found that 60 to 70 p.c. of the acetylene was converted into hydrocyanic acid. Gruszkiewicz (Zeitsch. Elektrochem. 1903, 9, 83) found that a mixture of carbon monoxide (2 vols.) hydrogen (1 vol.) and nitrogen (1 vol.) yielded small quantities of hydrocyanic acid when exposed to induction sparks between platinum points. Lipinsky (Zeitsch. Elektrochem. 1911, 17, 761) passed mixtures of methane, nitrogen and hydrogen through a 2200 volt alternating current arc between platinum electrodes. No carbon was deposited from a mixture containing CH (20 p.c.), H_2 (10 p.c.), and N_2 (70 p.c.). Under the best conditions about 1·75 gram of hydrocyanic acid was produced per kilowatt hour. It is instructive to compare this with the 50 grams of nitric acid per kilowatt hour which Raleigh obtained, in apparatus of comparable dimensions, from mixtures of oxygen and nitrogen.

E. Briner and A. Baerfuss (Helv. Chim. Acta. 1919, 2, 663) have obtained as much as 7·39 grams HCN per kilowatt hour by circulating 8–10 litres per hour of a mixture of 1 part methane and 5 parts nitrogen through an arc at 505 volts between platinum electrodes 12 mm. apart.

According to H. Philipp (Chem. Met. Eng. 1920, 22, 213), Lipinski's process was tried on a commercial scale in 1914 at Neuhausen, and a yield of 30 grams of HCN per kilowatt hour attained.

Hutton and Smith (Eng. Pat. 23835 of 1906, and Trans. Amer. Electrochem. Soc. 13, 359, 1908) showed that the temperature of the arc is not necessary, hydrocyanic acid being formed when a carbon rod is heated in a mixture of hydrogen and nitrogen to 1700°; and H. v. Wartenberg (Zeitsch. anorg. Chem. 52, 299, 1907) carried out quantitative measurements with the following results (using a mixture of equal volumes of hydrogen and nitrogen) :—

Temperature	P.c. HCN in the gas in equilibrium
1635°	1·95
1752°	3·10
1875°	4·70

Wallis (Annalen, 1906, 345, 353), by passing the same mixture through the electric arc at varying rates obtained a maximum of 33·5 p.c. of HCN in the gas. The estimated temperature of the arc is about 3250°.

Cyanides from nitrides. At high temperatures, nitrogen combines directly with several elements to form nitrides, and these, when fused with sodium carbonate and carbon, produce sodium cyanide. This has been shown to be the case with the nitrides of boron, calcium, magnesium, titanium, silicon, and aluminium, and with phospham PNH_2. Since none of these processes has emerged as yet from the experimental stage, it is sufficient to mention the possibility of producing cyanides in this way.

Hydrocyanic acid. Prussic acid (Ger. Blausäure). HCN.

This substance was discovered by Scheele in 1782 (Chemical Essays, London, 1786; reprinted 1901). He observed that Lixivium sanguinis loses its power of forming Prussian blue when it is exposed to the air, and traced this effect to the atmospheric carbon dioxide. Other acids also produced it, and the blue-forming principle was found in the vapour given off. By distilling

the *lixivium* with sulphuric acid, he obtained an aqueous solution of hydrocyanic acid. A more convenient method of preparation was to heat potassium ferrocyanide with dilute sulphuric acid. In doing this, he obtained a blue residue (oxidised Everitt's salt or Williamson's blue). Finally, he prepared mercuric cyanide by boiling Prussian blue with mercuric oxide; by heating this with iron and sulphuric acid, he decomposed it into mercury and hydrocyanic acid, which he distilled off. In 1783, Scheele found that hydrocyanic acid is inflammable, its combustion yielding carbon dioxide. He also proved that it contains nitrogen by synthesising it from ammonia. Equal parts of charcoal and potassium carbonate were heated to redness, but not sufficiently to melt the potash, in a crucible and then some ammonium chloride stirred in (for 2 minutes only); the mass was then thrown into water and a solution obtained which gave 'a great quantity of Prussian blue,' whereas a similar experiment without the sal-ammoniac yielded a very small quantity.

The exact quantitative composition of prussic acid was ascertained by Gay-Lussac (*Annales de Chimie*, 1815, 95, 156). He showed that it is similar in constitution to hydrochloric and hydriodic acids, the hydrogen being united with a compound radical, CN, which he called '*cyanogène*,' which plays the part of an element in so far as it passes through many transformations unchanged.

Compounds of hydrocyanic acid are widely distributed in nature in plants. The acid does not exist as such in the living plants, but is liberated after their death by the hydrolytic action of an enzyme on a glucoside, both of which are contained in the living cells; the glucoside may also be split up by boiling with dilute acids. Rarely a glucoside is found without an accompanying enzyme, as in the leaves of the common elder (*Sambucus niger*). The chemistry of the cyanogenetic glucosides is described under GLUCOSIDES. Very different quantities of hydrocyanic acid are obtained from different parts of the same plant, the quantity also depends on the age of the plant (it is usually greatest in the young plants) and on the conditions of growth such as climate and rainfall; the use of nitrogenous fertilisers has been found to increase the quantity of hydrocyanic acid present. Plants rarely yield as much as one or two tenths of 1 p.c. of their weight of hydrocyanic acid; for example: great millet (*Sorghum vulgare*) 0·013 to 0·044 p.c. in young plants, an exceptional North American sample gave 0·114 p.c.; wild cherry (*Prunus padus*) 0·03 p.c.; cherry laurel (*Prunus laurocerasus*) up to 0·2 p.c. in young leaves; cassava, sweet, 0·016 p.c. in the leaves, 0·043 p.c., in the peel of the stem, 0·005 p.c. in the edible part of the root, the corresponding parts of the bitter variety contained 0·041 p.c., 0·113 p.c., and 0·053 p.c. respectively; Rangoon beans (*Phaseolus lunatus*), 0·025 p.c.; linseed, 0·02 to 0·038 p.c.; *Nandina domestica*, 0·07 to 0·147 p.c.; bitter almonds 0·12 to 0·18 p.c. Cases of cattle poisoning are not infrequent in hot countries where sorghum is used as fodder, and linseed meal and white clover are also sometimes poisonous. The enzymes are de-stroyed and the cyanogenetic glucosides rendered harmless by thorough boiling with water.

Minute traces of hydrocyanic acid have been observed in the products of incomplete combustion, for example, in the luminous flame of a Bunsen burner, in boiler flue gases, and in tobacco smoke.
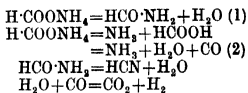
Preparation of Hydrocyanic Acid.—Hydrocyanic acid was formerly prepared by distilling potassium ferrocyanide with dilute sulphuric acid. A more convenient method, however, is to run a solution of sodium cyanide (97 to 98 p.c. NaCN) in from 2–2½ times its weight of water into hot sulphuric acid of 75 p.c. strength; about 1½ mols. of sulphuric acid to 2 mols sodium cyanide is sufficient and the cyanide solution is preferably allowed to enter the acid a little below its surface, so as to avoid contact of the alkaline cyanide solution with hydrocyanic acid vapour.

The vapour may be dried by calcium chloride, kept at a temperature of about 30° and then condensed in a vessel cooled by ice, although the greater part of it is quite readily liquefied in an ordinary Liebig's condenser cooled by cold water. It may be purified from traces of water and ammonia by distillation over phosphorus pentoxide (Nef, *Annalen*, 1895, 287, 265).

Hydrocyanic acid is formed in many different ways; the synthesis from free nitrogen and acetylene has already been mentioned. *The oxidation of organic compounds* by nitric acid often yields hydrocyanic acid in greater or smaller amount, and it has been proposed to manufacture hydrocyanic acid in this way. The interesting reaction described by Huntingdon (Eng. Pat. 14855, 1895) may be mentioned here. A mixture of acetylene and nitric oxide is readily exploded by a spark, yielding very considerable quantities of hydrocyanic acid in accordance with the equation

$$2NO + 2C_2H_2 = 2HCN + 2CO + H_2$$
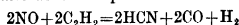
When *ammonium formate* is distilled, water is first given off together with a little ammonia and formic acid; at 180° formamide begins to distil over, and, as the temperature gradually rises to 220°, this is accompanied by increasing quantities of carbon monoxide, but only traces of hydrocyanic acid are produced. In order to obtain a good yield of hydrocyanic acid, the vapour must be heated to much higher temperatures, and the result is greatly influenced by the nature of the substance with which it is in contact. According to unpublished experiments by the writer, the principal changes which occur are:—

$$H \cdot COONH_4 = HCO \cdot NH_2 + H_2O \quad (1)$$
$$H \cdot COONH_4 = NH_3 + HCOOH$$
$$\qquad\qquad = NH_3 + H_2O + CO \quad (2)$$
$$HCO \cdot NH_2 = HCN + H_2O$$
$$H_2O + CO = CO_2 + H_2$$

The ammonia and hydrocyanic acid in the product usually accounted for more than 95 p.c. of the nitrogen in the ammonium formate or formamide used. Under similar conditions, the yield of hydrocyanic acid obtained from formamide is much greater than that obtained from ammonium formate. For each contact substance there is a certain temperature at which the yield is a maximum. The following table

contains the best temperatures and correspond-
ing yields for several contact substances :—

| Contact substance | Ammonium formate | | Formamide | |
	Yield of HCN p.c. of theoretical	Temperature	Yield of HCN p.c. of theoretical	Temperature
Porcelain chips	41·5	700°	75	800°
Copper gauze	43·0	just below 500°	78	600°
Iron wire	39·0	just below 500°	—	—
Charcoal	21·0	420°	55	400°

With finely divided nickel, no hydrocyanic
acid was obtained in any circumstances; at
273°, 92½ p.c. of the nitrogen was recovered as
ammonia, but much less at higher temperatures.

Formaldoxime $CH_2 : N \cdot OH$, an isomeride of
formamide, obtained by the interaction of
formaldehyde and hydroxylamine, decomposes
very readily when heated alone or with phos-
phorus pentoxide into water and hydrocyanic
acid (Dunstan and Bossi, Chem. Soc. Trans.
1898, 353).

Ammonia and carbon monoxide were said to
yield hydrocyanic when passed over heated
spongy platinum (Kuhlmann, Annalen, 1841,
38, 62), $CO+NH_3=HCN+H_2O$, and this ap-
parently simple reaction has attracted several
inventors. A careful investigation by Jackson
and Laurie (Chem. Soc. Trans. 1905, 87, 433) has
shown that a dry mixture of the two gases,
when sparked, treated by the silent discharge
or heated in presence of platinum (an electrically
heated spiral of platinum wire gives the best
result) yields ammonium cyanate thus :

$$CO+2NH_3=NH_4CNO+H_2$$
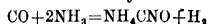
and Kuhlmann's reaction does not take place.
The reverse change, $HCN+H_2O=CO+NH_3$,
however, does occur very readily, even at 200°,
when a mixture of steam and hydrocyanic acid
is passed over broken brick as contact material,
and at 600° it is practically quantitative. With
iron oxide as contact substance, the conversion
into ammonia is complete at 285°, and with
Weldon mud at 200° (Carpenter and Linder, J.
Soc. Chem. Ind. 1905, 63).

Cyanogen and hydrogen combine, forming
hydrocyanic acid when a mixture of them is
heated at 500°–550° (Berthelot, Ann. Chim.
Phys. 1879, [5] 18, 380).

Properties of Hydrocyanic Acid.—A colourless
liquid possessing a characteristic smell (or rather
taste), which produces a choking sensation in the
larynx. It is one of the most poisonous sub-
stances known, the fatal dose for a full-grown
man being about 0·06 gram of the acid or 0·15
gram of potassium cyanide. It may be absorbed
through all parts of the body, even through the
skin, and its action is very rapid, large doses
causing death almost instantaneously. Air in
which the smell of hydrocyanic acid is distinctly
perceptible may be breathed constantly with-
out ill effects. Experiments with cats showed
that 3 to 4 volumes of the acid per 100,000
volumes of air could be borne, but 5 volumes

produced symptoms of poisoning. In industrial
cases of hydrocyanic acid poisoning the persons
affected were usually working in confined spaces,
for example, cleaning or repairing apparatus
which had contained cyanides, removing
damaged cargo from the holds of ships, or work-
ing in insufficiently ventilated buildings where
cyanide solutions were used; in all these cases
hydrocyanic acid is generated from alkali cyanide
solutions partly by hydrolysis and partly by
the action of carbon dioxide.

The first symptoms of poisoning are giddi-
ness and darkness of the visual field (these
symptoms disappear after a few minutes ex-
posure to fresh air), they are followed by un-
consciousness accompanied by muscular cramps
and more or less complete cessation of respira-
tion; the heart still acting, however, artificial
respiration with oxygen may be successful at
this stage. When a cyanide has been swallowed,
hydrocyanic acid is liberated by the acids of the
stomach. The simplest and most effective
antidote is prepared by mixing solutions of
ferrous sulphate and sodium carbonate (suitable
quantities are 50 c.c. each of solutions containing
150 grams of $FeSO_4, 7H_2O$ and 57 grams of
Na_2CO_3 per litre). Stimulants, such as ammonia,
are also helpful. The writer has seen a dog,
which had swallowed some potassium cyanide,
and was already partially paralysed in its hind
quarters, recover in a few seconds when dosed
with the above mixture which had been made
up hastily from ferrous ammonium sulphate.
Subcutaneous injection of hydrogen peroxide,
which converts hydrocyanic acid into oxamide,
has also been recommended.

The action of hydrocyanic acid appears to
consist partly of a direct effect on the nerve
centres and partly of an inhibitory action on
the enzyme of the red blood corpuscles, which
brings about the transference of oxygen from
oxyhaemoglobin to the oxidisable substances
in the body; the venous blood therefore becomes
arterial, and death is due partly to a kind
of internal suffocation. Schönbein (J. pr.
Chem. 1868, 105, 202) showed that hydro-
cyanic acid inhibits the catalytic decomposition
of hydrogen peroxide by plant ferments, and
also by the red blood corpuscles, and suggested
that its poisonous properties might be due to
the inhibition of the oxidising power of the
blood. Bredig and von Berneck (Zeitsch. phys.
Chem. 1899, 31, 329) showed that hydrocyanic
acid has the same effect on the inorganic ferment,
colloidal platinum. The ferments recover their
activity when the hydrocyanic acid is removed.
This property has been applied in the preserva-
tion of fruit.

The sp.gr. of the liquid acid is 0·7058 at 7°
and 0·6969 at 18° (Gay Lussac). Freezing-point,
−10° to −12° (Nef.). The freezing-point is
raised by pressure; it is −2·88° under 500 kilos
per sq. cm. and +50·1° under 4000 kilos per sq.
cm. pressure (Tamman). The boiling-point at
atmospheric pressure is 25° (Nef.). The heat of
evaporation is exceptionally large, 210·7 Cals.
per gram. Heat of formation of the liquid acid
from the elements (amorphous carbon) −21·8
Cals. per mol. (Thomsen), diamond −24·8 Cals.
(Berthelot). Heat of solution, liquid acid in
water, 0·4 Cal. per mol. The dielectric constant
of hydrocyanic acid, 95, is the largest known,

with the exception of that of hydrogen peroxide (Schlundt). The acid is miscible in all proportions with water, alcohol, ether and many other substances; it is almost insoluble in light petroleum. It is an excellent solvent for many solid substances; among the inorganic salts the iodides are usually readily soluble. The solutions are good conductors of electricity, the conductivity of solutions of potassium iodide, for example, is about 3½ times greater than that of the corresponding aqueous solutions.

Hydrocyanic acid is one of the weakest acids; its dissociation constant in aqueous solution at 18°, 1 3 × 10⁻⁹, is 44 times smaller than that of sulphuretted hydrogen, and 230 times smaller than that of carbonic acid (Walker and Cormack, Chem. Soc. Trans. 77, 16, 1900). In a 0·1N-solution, only 0·011 p.c. of the acid is dissociated into its ions, consequently it does not behave as an acid to indicators, and its salts are more or less completely decomposed by water; thus for example,

$$KCN + H_2O \rightleftarrows KOH + HCN$$

In 0·1 N-solutions of the sodium or potassium salts, 1·1 p c. is dissociated in this way; in N-solutions, only 0·3 p.c. at 24·2° (Shields, Zeitsch. physikal. Chem. 12, 167, 1893). In solutions of pure sodium cyanide, containing no caustic soda, the hydrolysis is greater than that found by Shields. It may be calculated from the equilibrium constant K = [HaOH][HCN∥NaCN], the bracketed quantities representing concentrations of the substances in gram mols. per litre. The values of K × 10⁴ are: at 0°, 0 135; at 5°, 0 15; at 10°, 0·16; at 15°, 0·20; at 20°, 0·27; at 25°, 0·484; and at 30°, 0·72 (F. P. Worley and V. R. Browne, Chem. Soc Trans. 1917, 1057). This is of importance when it is required to concentrate an aqueous solution of a cyanide; the free hydrocyanic acid escapes until sufficient excess of the base has accumulated to reduce the hydrolysis to negligible proportions. In the case of weaker bases, the result is a considerable loss of hydrocyanic acid; with calcium cyanide, for example, the quantity of lime formed is greater than can be retained in solution, consequently equilibrium is never attained, and when such a solution is evaporated, the whole of the hydrocyanic acid escapes, leaving a residue of pure lime.

A large part (sometimes one-half) of the cyanide used in gold extracting is lost by the evaporation from the solutions of hydrocyanic acid set free by hydrolysis (H. A. White, J. Chem. Met. and Min. Soc. S. Africa, 1915, 16, 24).

Pure hydrocyanic acid, distilled over phosphorus pentoxide, can be preserved without change for considerable periods at the ordinary temperature; when heated to 100° or at the ordinary temperature in presence of alkaline impurities, such as ammonium or potassium cyanide, it changes into a solid, black mass from which a ter-molecular polymer, probably the nitrile of amino malonic acid, NH₂·CH(CN)₂, can be separated. Under imperfectly known conditions, the anhydrous acid sometimes explodes. G. Salomone (Gazz. chim. ital. 1912, 42, i. 617) isolated, from the products of an explosion, colourless crystals of a substance having the composition of cyanic acid and a

molecular weight, in benzene solution, corresponding with (HCNO)₅.

The aqueous acid also becomes brown rapidly in presence of alkali cyanides and deposits a dark brown amorphous substance, azulmin or azulmic acid, which contains carbon, oxygen, nitrogen, and hydrogen in variable proportions. The discolouration of solid alkali cyanide, when exposed to the air, is due to the hydrocyanic acid liberated at its surface undergoing this change.

The only useful *application of hydrocyanic acid*, as an insecticide, was developed at the Agricultural Experiment Station of the University of California, largely by the labours of D. W. Coquillett and H. D. Bishop (California Station Bull. 122). They found that foliage is much less liable to injury at night than in sunlight; the hydrocyanic acid vapour is applied by erecting a tent over the trees and generating the acid inside of it. The safe concentration of hydrocyanic acid depends on the kind of tree and on the time of year. In greenhouses less than 2 grams of hydrocyanic acid per 1000 cb. ft. of air space is said to kill green aphis, but as much as 30 grams may be needed for mealy bug or red spider. Most plants are unaffected even by the larger quantity. Since about 1918 98 p.c. hydrocyanic acid has been placed on the market for the fumigation of orange trees; formerly the acid was always generated on the spot, from sodium cyanide and sulphuric acid.

The constitution of hydrocyanic acid has been the subject of much discussion arising largely from the observation that the reaction of potassium cyanide with an ester yields a nitrile, R—C⦂N, as principal product, whereas silver cyanide yields a carbylamine, R—N⦂C. On the hypothesis that the salts are formed by the substitution of an atom of metal for an atom of hydrogen without change of position, and that the alkyl derivatives are formed similarly, it is of course necessary to suppose that the hydrogen in hydrocyanic acid may be united either with carbon or with nitrogen The cyanides are, however, in all probability more complex substances; silver cyanide, from its mode of formation, is probably silver dicyano argentaate, Ag[Ag(CN)₂], and the reaction with methyl iodide is similar to that of silver ferrocyanide (described above) leading to the well-crystallised

substance $\left[Ag{CN \atop CNCH_3}\right]$, which, like the corre-

sponding ferrocyanide, splits off methyl carbylamine when heated or when acted on by a solution of potassium cyanide (see, for example, H. Guillemard, Ann. Chim. Phys. 1908, [8] 14, 311).

The properties of hydrocyanic acid itself, however, leave little doubt that it is formonitrile; the isomeric substance H·N⦂C, has not been isolated. Like the nitriles, hydrocyanic acid is hardly affected by dilute mineral acids (it is frequently separated quantitatively by distilling acid solutions); the carbylamines are violently decomposed. Anhydrous hydrocyanic acid and the nitriles do not dissolve silver cyanide, whilst the carbylamines dissolve it very readily. In its high dielectric constant, solvent and dissociating powers and physiological action hydrocyanic acid also resembles the nitriles rather

than the carbylamines (Wade, Chem. Soc. Trans. 1902, 1613).

THE PRINCIPAL CYANIDES.

Potassium cyanide KCN crystallises in anhydrous, colourless octahedra from aqueous solutions, or in cubes when the fused salt solidifies; sp.gr. 1·52. It melts at a dull red heat, and volatilises without decomposition at high temperatures It is readily soluble in water; the saturated solution contains 122·2 grams of KCN to 100 grams of water at its boiling-point (103·3°). At 19·5°, 100 grams of absolute alcohol dissolve 0·88 gram, 100 gr. methylalcohol dissolve 4·91 grams (Landolt, Börnstein and Meyerhoffer, Tabellen, Berlin, 1905). It is moderately soluble in anhydrous ammonia at −38° (Franklin and Kraus, Amer. Chem. J 1898, 20, 820). It deliquesces in moist air.

Sodium cyanide NaCN crystallises from the fused liquid in apparently cubic crystals; from aqueous solutions below 35° large colourless plates of the hydrate $NaCN,2H_2O$ are deposited. Joannis (Ann. Chim. Phys. 1882, [5] 26, 484) obtained a hydrate $NaCN,\frac{1}{2}H_2O$ from cold 85 p.c. alcohol. F. Roessler (Eng. Pat. 279, 1899) showed that the hydrate $NaCN,2H_2O$ decomposes at 33° (34·7° according to the writer's measurements) into the anhydrous salt and a saturated solution, about 40 p.c. of the sodium cyanide separating in the anhydrous state. The solubility of the hydrate (in grams of NaCN to 100 grams of water) is, 35·4 at −20°; 43·4 at 0°; 58·3 at 20° and 82 at 34·7°. The solubility of the anhydrous salt is almost independent of the temperature (82 grams per 100 grams of water). Sodium cyanide appears to be more soluble in ethyl and methyl alcohol and anhydrous ammonia than the potassium salt. The sp.gr. of aqueous solutions of sodium cyanide at 25° is given by the expression $1+0·00534p$, where p is the percentage of NaCN. Sodium cyanide (96 p.c.) melts at 540°. The pure salt, when heated in a glass tube so as to be out of contact with metals, in a current of dry air free from carbon dioxide, remains entirely unchanged at temperatures up to 370°; if, however, it is in contact with iron or nickel, or if traces of the oxides of these metals are added to it, oxidation proceeds rapidly, cyanate and carbonate being formed and carbon dioxide evolved. The carbonate is formed by the oxidation of the cyanate, which is the primary product. Sodium cyanate behaves towards oxygen in exactly the same way as the cyanide; it is quite unaffected by dry air (free from CO_2) even at 400°, but when mixed with 1 p.c. of nickel oxide it oxidises rapidly; thus :

$$2NaCNO+3O=Na_2CO_2+CO_2+N_2$$
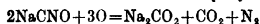
(writer's unpublished statement).

Sodium cyanide absorbs moisture with great avidity from ordinary moist air. The writer has found that it takes up water from purified air saturated with aqueous vapour at 20° at all temperatures below 44°, but not at higher temperatures. This is of importance in sampling and analysing the salt.

Dilute solutions of potassium or sodium cyanide decompose slowly in contact with the air, the loss being due to evaporation of the hydrocyanic acid formed by hydrolysis, which permits the decomposition to proceed further; absorption of carbon dioxide acts in the same direction by neutralising the caustic alkali.

Liebig's statement that metallic iron is dissolved by hot solutions of potassium or sodium cyanide with evolution of hydrogen is true of the finely divided metal, but iron vessels may be used for years for boiling concentrated solutions of cyanides without requiring repair, and iron tanks are regularly used in the treatment of gold ores with cyanide solutions.

With the exception of lead and platinum, all ordinary metals are dissolved by cyanide solutions in presence of oxygen.

Zinc is slowly dissolved without oxygen, but if a piece of zinc is half immersed in a cyanide solution, it is eaten through at the surface of the liquid before any appreciable action has taken place on the submerged portion.

Alkali cyanides yield ammonia and a formate when boiled with water or treated with strong sulphuric acid; in the latter case the formic acid produced is at once decomposed into carbon monoxide and water.

Mercuric cyanide $Hg(CN)_2$ was first prepared by Scheele, in 1782, by boiling Prussian blue with mercuric oxide, and, in 1783, by dissolving mercuric oxide in hydrocyanic acid and evaporating to crystallisation. He also found that mercurous salts, when treated with soluble cyanides, yield mercuric cyanide and metallic mercury. The decomposition of the ferrocyanides, as already mentioned, depends on the extremely small electrolytic dissociation of mercuric cyanide in aqueous solution. For the same reason, it is not decomposed by caustic alkalis, and hydrocyanic acid can only be expelled from it by boiling with a strong acid. The concentration of the mercury ions is, however, sufficient to permit of the precipitation of the extremely insoluble mercuric sulphide by sulphuretted hydrogen.

Mercuric cyanide crystallises in anhydrous, colourless crystals of sp.gr. 4·0. The saturated solution contains 93 grams per litre at 20°, 111 grams per litre at 25°; 100 grams of absolute alcohol dissolve 10·1 grams of it at 19·5°, and 100 grams of absolute methyl alcohol take up 44·2 grams at 19·5°.

Small quantities of mercuric cyanide are sometimes used in addition to alkali cyanide in the treatment of ores containing silver sulphide (Clennel, Cyanide Handbook, London, 1910, 297), the dissolution of which is accelerated, probably owing to the formation of mercuric sulphide :

$$Hg(CN)_2+Ag_2S+2KCN=HgS+2KAg(CN)_2$$

Calcium cyanide has never been prepared in the pure state. An aqueous solution of lime in hydrocyanic acid decomposes completely into its constituents when boiled (Scheele). By evaporating such a solution in vacuo, Joannis obtained a crystalline compound, $3CaO·Ca(CN)_2,15H_4O$, which decomposed completely in a vacuum, leaving nothing but lime. Dry reactions, at high temperatures, yield calcium cyanamide, but no cyanide.

Barium cyanide $Ba(CN)_2$. When a concentrated solution, made by adding hydrocyanic acid to baryta in theoretical quantities, is evaporated in vacuo, crystals of the hydrate

$Ba(CN)_2.2H_2O$ are deposited (A. Joannis, Ann. Chim. Phys. [5] 26, 484, 1882). This is a very deliquescent substance which, when dried *in vacuo* over sulphuric acid, yields an amorphous monohydrate which can be completely dehydrated by heating it very gradually to 100° in a good vacuum. The writer has failed to obtain a pure product in this way. Some 7 or 8 p.c. of the hydrocyanic acid escapes during evaporation, and the product contains a corresponding quantity of barium hydroxide. By drying pure $Ba(OH)_2,8H_2O$ in a good vacuum at 100°, a very finely divided powder of $Ba(OH)_2$ is obtained which is suspended in dry light petroleum and treated with a small excess of dry hydrocyanic acid also mixed with light petroleum. In this way, the solid hydrated barium cyanide is obtained without evaporation :

$$Ba(OH)_2 + 2HCN = Ba(CN)_2,2H_2O$$
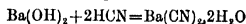
When dehydrated *in vacuo*, it still contains a little hydroxide, but by shaking it with a little hydrocyanic acid and light petroleum and again drying, practically pure anhydrous barium cyanide is fairly easily obtained.

By saturating a solution of baryta in methyl alcohol with hydrocyanic acid, a compound $Ba(CN)(OCH_3) + CH_3OH$ is obtained, which, when heated, first loses methyl alcohol and then methyl ether, leaving $BaO + Ba(CN)_2$ (Drechsel, J. pr. Chem. [2] 21, 77, 1880).

Dry methods of preparation yield mixtures of cyanide and cyanamide. When barium ferrocyanide is heated it begins to decompose about 500°, yielding a mixture of barium cyanide and cyanamide (with carbon and iron) in which nearly 60 p.c. of the nitrogen is in the form of cyanamide, practically the same product as that obtained by the action of nitrogen on barium carbide. Even the action of cyanogen on barium amalgam yields a mixture (Drechsel), the reason being that barium cyanide decomposes into barium cyanamide and carbon, thus : $Ba(CN)_2 = BaCN_2 + C$. The change is very slow at 500° to 600°, but it is accelerated by iron (Ewan and Napier, J. Soc. Chem. Ind. 1913, 32, 467).

Barium cyanide is colourless ; 100 grams of cold water dissolve about 80 grams of it (Joannis). It melts about 600°. It is distinctly volatile, even at its melting-point, but when mixed with barium oxide it is much less so.

Silver cyanide AgCN. The precipitate obtained by adding excess of silver nitrate to a solution of a soluble cyanide is probably the silver salt of the complex acid $H[Ag(CN)_2]$. The solubility of silver cyanide in pure water lies between those of the chloride and sulphocyanide, as the following table shows :—

	Solubility at 25° in gram-mols. per litre
AgI	0.01×10^{-6}
AgBr	0.81×10^{-6}
AgSCN	1.08×10^{-6}
AgCN	4.40×10^{-6}
AgCl	14.10×10^{-6}

It is hardly attacked by cold dilute nitric acid, but is decomposed quantitatively on boiling (Plimmer, Chem. Soc. Proc. 1903, 285). When dry silver cyanide is heated about one-half of the CN is given off in the form of

cyanogen C_2N_2. Further heating in presence of oxygen yields a residue of metallic silver, which usually contains a little carbon. It is slightly soluble in a solution of hydrocyanic acid, forming the unstable acid $HAg(CN)_2$. It dissolves very readily in alkali cyanides to salts such as $KAg(CN)_2$, in which the silver is contained in the complex anion $Ag(CN)'_2$. Owing to the excessively small dissociation of this anion, all silver salts except the sulphide are dissolved by cyanide solutions, and in presence of oxygen, metallic silver and the sulphide are also dissolved.

Gold cyanides. Aurous cyanide and the soluble aurocyanides are of technical importance. The former, AuCN, a yellow crystalline powder, insoluble in water and acids, is formed by the action of hydrocyanic acid on auric hydroxide. It is readily soluble in solutions of alkali or alkaline-earth cyanides, yielding aurocyanides such as $KAu(CN)_2$. A solution of the potassium salt, which is used for electroplating with gold, is readily obtained by precipitating a solution of gold chloride with ammonia and dissolving the fulminating gold in a solution of potassium cyanide, or by precipitating gold chloride with magnesia, dissolving out the excess of magnesia in the precipitate with nitric acid, and then dissolving the auric hydroxide in potassium cyanide as before.

Potassium aurocyanide is also formed when gold is dissolved in a solution of potassium cyanide in presence of oxygen or other oxidising agent :

$$4KCN + 2Au + O + H_2O = 2KAu(CN)_2 + 2KOH$$
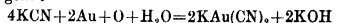
(Clennel, Cyanide Handbook, 1910, 10–32 gives a full account of the discovery of this reaction.)

The dissolution of metallic gold is primarily due to the great stability of the aurocyanogen ion $Au(CN)_2'$. Metals, like all other substances, have a tendency to dissolve in water. In contact with its aqueous solution, a salt will dissolve if the solution is unsaturated, or crystallise out if it is supersaturated. Metals behave similarly, with the important difference that they dissolve in the form of positively charged *ions*, so that when a metal is placed in contact with a solution containing fewer of its ions than correspond with equilibrium, it gives out positively charged atoms, becoming itself negatively charged, until the electrical attraction stops further change, and *vice versâ*. In this way, a definite potential difference always arises between a metal and a solution of it, the sign and magnitude of which depend on the nature of the metal and on the concentration of the positively charged ions of the metal in the solution.

In order for a metal to dissolve at all, therefore, it is necessary that the solution shall contain less than the saturation quantity of positive ions ; and for the dissolution to continue, the positive charges of the ions and the negative charge of the metal must be got rid of in some way.

These conditions are fulfilled in the case of the dissolution of gold in a cyanide solution containing oxygen, because the dissociation of the complex ion, $Au(CN)_2' \rightleftarrows Au^{.} + 2CN'$ is extremely small, and solutions of it therefore contain infinitesimal quantities of gold ion, and further the electrical charges produced by the

dissolution of the gold are removed by the reactions:

$$Au^{\cdot}+2(CN)'=Au(CN)'$$

and

$$O+H_4O+2(-)=2OH'$$
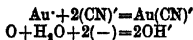
the result of which, written in the ionic form, is

$$4K^{\cdot}+4(CN)'+2Au^{\cdot}+O+H_2O+2(-)$$
$$=4K^{\cdot}+2Au(CN)_2'+2OH'$$

The potential difference between a metal like zinc (which has a greater tendency to dissolve than gold) and a cyanide solution is much greater than the natural potential difference between gold and the solution; hence gold ions are drawn out of the solutions to the zinc, where their positive charges are neutralised by the negative charge of the zinc. This disturbs the equilibrium between zinc and the solution and also between zinc and aurocyanogen ions and gold ions, causing fresh quantities of zinc to dissolve and of aurocyanogen ions to dissociate, processes which continue until the whole of the gold is precipitated.

As W. Skey (Trans. and Proc. New Zealand Inst. 8, 334, 1876) first showed, gold in cyanide solutions is electro-positive to silver and silver to mercury, so that gold will precipitate silver and mercury from their solutions in cyanides. This has been confirmed by Bodländer (Ber. 1903, 36, 3933). This reversal of the usual order is, as will be understood from the above explanation, due to the increasing stability of the mercury, silver, and gold complex cyanogen ions.

It is of interest to note that most of the minerals which accompany gold in its ores are electro-negative to gold in cyanide solutions, and therefore accelerate its dissolution in the way which is familiar in the solution of zinc in sulphuric acid in presence of copper or platinum.

Barium platinocyanide $BaPt(CN)_4.4H_2O$ is most readily made by electrolysing a solution of barium cyanide (270 grams per litre) with platinum electrodes and an alternating current (0·4 ampere per sq. cm.), about 0·6 gram platinum is dissolved per ampere hour. After removing the excess of barium by CO_2 the solution is concentrated to crystallisation (A. Brochet and J. Petit, Bull. Soc. chim. 1904, [3] 31, 630). The salt crystallises in monoclinic prisms, which are yellow by transmitted, violet-blue by reflected, light. It dissolves in 33 parts of water at 16°. By recrystallisation from a solution containing barium cyanide it is obtained in small crystals which are highly fluorescent when exposed to X-rays, and are suitable for making fluorescent screens for X-ray work.

Copper cyanides. When potassium cyanide is added to the solution of a cupric salt, a brownish precipitate of cupric cyanide $Cu(CN)_2$ is produced, which gradually evolves cyanogen, changing into green cupric cuprous cyanide. When heated, this loses a further quantity of cyanogen and yields white cuprous cyanide CuCN, the constitution and reactions of which appear to resemble those of silver cyanide.

Cuprous cyanide is soluble in solutions of potassium cyanide, about 2½ molecules of KCN being required to dissolve 1 molecule of CuCN; the solutions contain the complex anions $Cu(CN)_3''$ and $Cu(CN)_4'''$ (Kunschert, Zeitsch. anorg. Chem. 41, 359, 1904). These anions are so little dissociated into copper ions that sul-

phuretted hydrogen will not produce a precipitate in the solutions, and therefore copper itself (in presence of oxygen) and all its compounds dissolve readily in cyanide solutions. Solutions of the sodium or potassium cupro-cyanides are used in the electro-deposition of copper on iron.

Zinc cyanide $Zn(CN)_2$ is a white substance, insoluble in water, but soluble in acids and in cyanide solutions. It is not easily prepared in a perfectly pure condition, because water decomposes it partially. When dry it is very stable, decomposing only at a bright-red heat.

The complex salt potassium zinc cyanide $K_2Zn(CN)_4$ crystallises in large well-formed octahedra from aqueous solutions; 100 grams of water at 20° dissolve 11 grams of it. It is anhydrous, and may be fused at a red heat without decomposition. The sodium salt $NaZn(CN)_3.2\frac{1}{2}H_2O$ is very readily soluble in water. The complex zinc cyanogen ions are much less stable than those containing copper, gold, silver, and mercury; a small excess of an alkali sulphide precipitates the zinc completely.

Cyanogen (Ger. Cyan) C_2N_2 was discovered by Gay-Lussac. It is prepared by heating perfectly dry mercuric cyanide at a dull red heat, $Hg(CN)_2=Hg+C_2N_2$. A part of the cyanogen is always polymerised to dark-brown, non-volatile paracyanogen. Paracyanogen appears to be the stable form at ordinary temperatures, at high temperatures it is converted into cyanogen. The velocity of the change is very small at temperatures below 300°, so that cyanogen gas can exist in the cold without change.

Cyanogen itself is a gas which burns with a peach-blossom-coloured flame. Liquid cyanogen boils at −20·7° under atmospheric pressure and freezes at −34·4°. Its critical temperature and pressure are 128·3° and 59·6 atmos. respectively (Cardoso and Baume, Compt. rend 1910, 151, 141). Its heat of formation from graphite and nitrogen is 70,000 cals. per molecule. Water dissolves 4·95 times its volume of the gas at 0°. At 18° the dissolved cyanogen is hydrolysed to hydrocyanic and cyanic acids, the latter yielding ammonia and carbon doxide so that no definite solubility is observed (Naumann, Zeitsch. Elektrochem. 16, 772, 1910). After some time the solution deposits dark brown azulmic acid and contains also oxalic acid and urea. Cyanogen dissolves in caustic alkalis, yielding cyanide and cyanate: $2KOH+C_2N_2=KCNO+KCN+H_2O$. Silver nitrate solution has no action on it. By means of these two reactions, it may be separated from hydrocyanic acid and estimated quantitatively in mixtures of the two gases (Wallis, Annalen, 345, 353, 1906). Cyanogen is very poisonous.

A knowledge of the exact conditions under which cyanogen can be formed from its elements is of interest in the theory of several technical processes for the manufacture of cyanides.

Wallis loc. cit. has shown that the electric arc burning between electrodes of very pure carbon in an atmosphere of nitrogen produces no cyanogen at all. H. v. Wartenberg (Zeitsch. anorg. Chem. 52, 299, 1907) pointed out,- however, that a very intense cyanogen spectrum is seen, and that carbon is deposited at some distance from the arc. Nernst's theorem indicates that very considerable

quantities of cyanogen should exist in equilibrium with carbon and nitrogen at the temperature of the arc :

Temperature	Per cent. C_2N_2 in the gas calculated from Nernst's theorem
2000°	0·01
2500°	0·9
3000°	17·0
3250°	45·0

The probable explanation is that cyanogen is essentially unstable at low temperatures ; that it can exist at all is due to an excessively slow rate of decomposition. Berthelot (Force des Matières Explosives, Paris, 1883, 113) has shown that it can be detonated by mercury fulminate, and, when heated, its rate of decomposition becomes measurable at 1200°. v. Wartenberg supposes, therefore, that cyanogen is really formed at the high temperature, but that it decomposes again completely before it can cool to temperatures at which it can continue to exist. It is obvious from the figures given above that the direct union of carbon and nitrogen to cyanogen can play no part in the formation of cyanides in processes which are carried out at ordinary furnace temperatures.

Cyanogen chloride CNCl is formed by the action of chlorine on mercuric cyanide (Serullas, Ann. Chim. Phys. 1827, 35, 291), zinc cyanide (A. Held, Bull. Soc. chim. 1897, [3] 17, 287), or aqueous hydrocyanic acid (Berthollet, 1787 ; A. Wurtz, Annalen, 1847, 64, 367). Alkali cyanides are unsuitable, because, except in cold, very dilute solutions, they react violently with cyanogen chloride, yielding dark-brown, amorphous products. The preparation of cyanogen chloride in considerable quantities is described by T. S. Price and S. J. Green (J. Soc. Chem. Ind. 1920, 39). A 12 to 15 p.c. solution of pure hydrocyanic acid is treated with chlorine at about 40°, the slow absorption of chlorine is hastened by injecting it into the solution of a finely divided condition through porous earthenware. The cyanogen chloride distils off as it is formed, together with hydrocyanic acid, the product containing 10–20 p.c. of the latter. It is purified by retreatment with chlorine, or by shaking it with zinc oxide, which removes hydrocyanic acid almost completely. Hydrochloric acid is removed by distillation over sodium bicarbonate.

Cyanogen chloride is a colourless liquid, which boils at 12·66°, 760 mm., and solidifies at −8°. Its vapour pressure (mm.) is : 68·3 at −30° ; 148·2 at −20° ; 270·5 at −10° ; 441·1 at 0° ; 681·9 at 10° ; 1001·9 at 20° ; 1427·4 at 30° ; 1988·0 at 40° ; 2719·3 at 50° ; 3664·2 at 60° ; 4873·2 at 70° (Regnault). The vapour attacks the eyes violently. The cold, saturated aqueous solution contains about 6 p.c. CNCl. The heat of formation of liquid CNCl from its elements is −26·9 cals. per molecule. Dry cyanogen chloride may be preserved indefinitely when pure ; in presence of hydrochloric acid it polymerises to cyanuric chloride $C_3N_3Cl_3$. Aqueous hydrochloric acid (stronger than about 2N) hydrolyses it thus :

$$CNCl + 2H_2O = NH_4Cl + CO_2$$
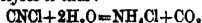
Its behaviour towards alkalis is the same as that of cyanogen bromide described below. Hydriodic acid hardly attacks it in the cold, and it is without action on metals, such as iron and copper, at ordinary temperatures.

Cyanogen bromide CNBr. A solution containing cyanogen bromide in addition to a cyanide dissolves gold more rapidly than one containing cyanide alone (Sulman and Teed, Eng. Pat. 18592, of 1894 ; and J. Soc. Chem. Ind. 1897, 961). Cyanogen bromide is therefore used in the treatment of a few refractory ores, the West Australian tellurides especially. The final result of the reaction is expressed by the equation : $2Au + 3KCN + BrCN = 2KAu(CN)_2 + KBr.$

Cyanogen bromide is formed by the action of bromine on a cyanide or on hydrocyanic acid. Owing to the difficulty of transporting either bromine or cyanogen bromide, it is always prepared at the place where it is to be used by liberating bromine from a mixture of a bromide and a suitable oxidising agent by the addition of sulphuric acid, and then adding a concentrated solution of an alkali cyanide. By the use of a suitable quantity of the oxidising agent, the whole of the bromine is utilised ; with sodium bromate, for example, the reaction is (C. Göpner, Zeitsch. angew. Chem. 1901, 14, 355) :

$$2NaBr + NaBrO_3 + 3NaCN + 3H_2SO_4 = 3Na_2SO_4 + 3BrCN + 3H_2O$$
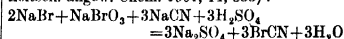
Cyanogen bromide is a colourless, crystalline substance, which melts at 52° and boils at 61° ; 100 grams of water dissolve from 5 to 6 grams of it at the ordinary temperature. It has an intensely irritating effect on the mucous membranes and eyes, and is said to be very poisonous. The perfectly pure substance can be kept without change, but traces of bromine (or hydrobromic acid) cause it to polymerise rapidly to cyanuric bromide, partial decomposition always occurring. It is very slowly decomposed by water : $CNBr + H_2O = HCNO + HBr$, the cyanic acid decomposing further to ammonia and carbon dioxide. Caustic alkalis bring about the same change instantaneously, alkali carbonates much more slowly, and bicarbonates have no action at all. Cyanogen bromide and potassium cyanide react in aqueous solution, yielding cyanogen ; thus :

$$CNBr + KCN = KBr + C_2N_2$$
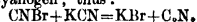
(private communication from Mr. C. J. Ellis). In solutions containing 0·2 to 0·8 p.c. of potassium cyanide and 0·1 to 0·2 p.c. of cyanogen bromide, the latter is completely decomposed in from 3 to 6 hours at the ordinary temperature.

In aqueous solution cyanogen bromide reacts with hydriodic acid and with sulphuretted hydrogen according to the equations :

$$CNBr + 2HI = HCN + HBr + I_2$$
and
$$CNBr + H_2S = HCN + HBr + S$$
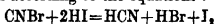
The first reaction provides a convenient method for the quantitative estimation of cyanogen bromide. Chattaway and Wadmore (Chem. Soc. Trans. 1902, 191) have shown that these reactions are characteristic of compounds in which the halogen atom is directly linked with nitrogen, and that cyanogen bromide therefore has the constitution C : N.Br.

Cyanamide NH₂·CN was first prepared by the action of ammonia on an ethereal solution of cyanogen chloride (Cloëz and Cannizzaro, Compt. rend. 1851, 32, 62) ; ammonium chloride crystallises out and cyanamide remains when the ether is evaporated. The same reaction

occurs in aqueous solution. The formation of the disodium salt, Na_2CN_2, by the action of sodamide on carbon or on sodium cyanide has already been described. The same substance is also produced when sodamide acts on sodium cyanate, sodium carbonate or carbon dioxide at a low red heat; it is also formed when either sodium cyanate or sodium cyanide is fused with sodium hydroxide.

The calcium and barium salts, $CaCN_2$ and $BaCN_2$, may be prepared from nitrogen and the carbides, by heating the corresponding ferrocyanide or by heating the carbamates or cyanates to redness (Drechsel, J. pr. Chem. 1877, [2] 16, 188; 1880, [2] 21, 77) thus:
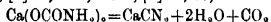
$$Ca(OCONH_2)_2 = CaCN_2 + 2H_2O + CO_2$$
and
$$Ca(OCN)_2 = CaCN_2 + CO_2$$

Cyanamide is also obtained by the action of mercuric oxide on a solution of thiourea:

$$CS(NH_2)_2 + HgO = NH_2CN + HgS + H_2O$$
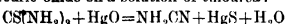
Several guanidine derivatives yield cyanamide when boiled with water or alkalis, for example, nitroso guanidine decomposes thus:

$$C\begin{matrix}\diagup NH_2 \\ : NH \\ \diagdown NH.NO\end{matrix} = C\begin{matrix}\diagup NH_2 \\ : N \\ \end{matrix} + N_2 + H_2O$$

(Thiele, Annalen, 1893, 273, 136).

Cyanamide is easily prepared from the di-sodium salt by neutralising its cold, aqueous solution with nitric acid, and evaporating to dryness on the water bath in a vacuum; the dry residue is extracted with ether. Werner (Chem. Soc. Trans. 1916, 1323) describes a convenient method of preparing it from the readily accessible calcium salt; 100 grams are mixed with 125 gr. of acetic acid and 120 gr. of water, the mixture well kneaded and left for 24 hours. The friable mass is then powdered and extracted with ether in a Soxhlet apparatus. Yield 94–96 p.c. of theory.

Cyanamide forms colourless, deliquescent crystals which melt at 43°–44° (E. Colson, Chem. Soc. Trans. 1917, 555), it is readily soluble in water, alcohol and ether, very sparingly soluble in carbon disulphide, benzene, and chloroform. When heated it polymerises very readily to dicyanodiamide, $NH_2.(C:NH).NH.CN$, it boils at 140° at 19 mm., much melamine being left behind; the neutral aqueous solution possesses considerable stability, but polymerisation occurs in presence of either acids or alkalis. The process has been studied carefully by Morrell and Burgen (Chem. Soc. Trans. 1914, 576) and by Grube and Krüger (Zeitsch. phys. Chem. 1914, 86, 65), who find that in alkaline solutions the reaction takes place between undissociated cyanamide molecules and cyanamide ions, $H_2CN_2 + HCN_2' = H_3C_2N_4'$. The rate of polymerisation is therefore a maximum when one-half of the cyanamide is in the ionised form, a condition which is practically attained when a quantity of a strong base (soda or lime) equivalent to one-half of the cyanamide is added, the salts of a weak base such as ammonia being largely hydrolysed, the necessary concentration of cyanamide ion is not readily attained, weak bases, therefore, have a much smaller polymerising action than strong ones.

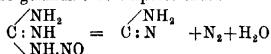The action of acids is more complicated, polymerisation and hydrolysis to urea occurring simultaneously. According to Carlson (Zeitsch. angew. Chem. 1914, 27, 724) cyanamide, treated with 10 to 20 p.c. sulphuric acid, is converted almost wholly into urea at the ordinary temperature, whereas near the boiling-point polymerisation predominates. In acid solutions the reaction is further complicated by the hydrolysis of the dicyanodiamide to dicyanodiamidine

$$NH_2.(C:NH)NH.CN + H_2O$$
$$= NH_2(C:NH).NH.CO.NH_2$$
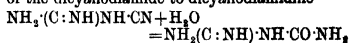
a strong base which neutralises the acid.

Cyanamide is an extremely weak acid, its dissociation constant, for $H_2CN_2 = H^+ + HCN_2'$ is of the order 10^{-11} (Grube and Krüger). The sodium salt $NaHCN_2$ crystallises from a solution of cyanamide in absolute alcohol when sodium ethylate is added to it, but the salt Na_2CN_2 can only be prepared by one of the dry fusion methods mentioned above. The calcium salt $CaCN_2$ also decomposes when treated with water yielding a solution of $Ca(HCN_2)_2$. The silver salt Ag_2CN_2 is a canary-yellow precipitate obtained by adding a solution of silver nitrate to a dilute ammoniacal solution of cyanamide; it is readily soluble in cold dilute nitric acid. The lead salt $PbCN_2$ is an orange-yellow precipitate. Cyanamide, also combines with acids; a white crystalline substance $H_2CN_2.2HCl$ is formed when dry hydrochloric acid is passed into a solution of cyanamide in dry ether (Mulder and Smit, Ber. 1874, 7, 1634).

Cyanic acid HCNO is prepared by distilling cyanuric acid (Wöhler) or by warming urea with phosphorus pentoxide (Weltzien, Annalen, 1858, 107, 219) and condensing the vapour at −18°. It is a volatile liquid, the smell of which resembles that of strong acetic acid. It is extremely unstable, changing rapidly even at 0° into the white amorphous polymeric substance cyamelide. The solution in dry ether is comparatively stable. The interesting relationship of cyanic acid HCNO, cyanuric acid

Temperature.
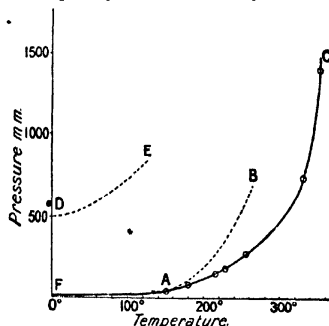
(HCNO)$_3$, and cyamelide (HCNO)x, has been studied by Troost and Hautefeuille (Compt. rend. 1868, 67, 1340), van't Hoff and van Deventer (Studies in Chem. Dynamics, 1896). The diagram represents the approximate relative positions of the vapour pressure curves of cyanic acid (HCNO), cyanuric acid (HCNO)$_3$, and cyamelide (HCNO)x, all of which yield the same vapour.

(The few points determined experimentally are indicated by small circles.) At the triple

point A (150° and 50 mm.) the two solid phases cyamelide and cyanuric acid coexist together with the vapour phase. Above 150° cyanuric acid is the stable phase (vapour pressure curve AC), at lower temperatures cyamelide (curve FAB) is stable. The position of the vapour pressure curve of cyanic acid itself (very roughly indicated by DE) shows that cyanic acid is quite unstable relatively to cyamelide. If the curve DE cuts the curve AB and AC the points of intersection would represent the melting-points of cyamelide and cyanuric acid respectively. They obviously lie at temperatures at which these substances decompose.

In aqueous solution cyanic acid is hydrolysed, slowly in cold dilute solutions, rapidly when warmed, to ammonia and carbon dioxide, $HCNO + H_2O = NH_3 + CO_2$.

The formation of cyanates by the action of cyanogen on alkalis, by oxidation of cyanides by the action of alkalis on cyanogen bromide, and from carbon monoxide and ammonia, has already been described.

Ammonium cyanate $NH_4 \cdot CNO$ is prepared in the form of a white snow, by mixing the vapours of cyanic acid and ammonia well diluted with an indifferent gas. When warmed it is converted into urea $NH_4CNO = CO(NH_2)_2$. The same reaction occurs in aqueous solutions, in which, however, it is reversible, 3·2 p.c. of the cyanate remaining unchanged at 32° and 65 p.c. at 100' (Walker and Hambly, Chem. Soc. Trans. 1895, 746).

Potassium and Sodium cyanates KCNO and NaCNO are easily prepared by grinding together the dry cyanides and the theoretically necessary quantity of lead oxide, and heating the mixture gently until the lead is melted. The salt is then recrystallised from water or dilute alcohol. According to Paterno and Pannain (Gazz. chim. ital. 1904, 34, ii. 152) when a solution of 4 to 6 mols. KCN and 1 mol. KOH per litre is electrolysed with 4–6 volts and 1–4 amps. per sq. dcm. of anode surface and the solution at the anode agitated, the cyanide is oxidised almost quantitatively to cyanate. J. Milbauer (Zeitsch. anorg. Chem. 1904, 42, 433) observed that potassium sulphocyanide, when heated at 300° with lead oxide, gave cyanate thus : $KSCN + PbO = KCNO + PbS$.

The decomposition of the alkali cyanates at high temperatures and their reduction by carbon are described above.

Potassium cyanate crystallises in thin transparent plates of sp.gr. 2·05, readily soluble in water, and anhydrous ammonia, insoluble in absolute alcohol, and fusible without decomposition below a red heat.

Sodium cyanate. 100 grams of water at 16° dissolve 10·68 grams; it fuses without decomposition about 500°. *Lead cyanate* is a crystalline precipitate, which is formed when solutions of a soluble cyanate and of a lead salt are mixed. The dry salt is stable, but it decomposes when boiled with water, yielding urea and lead carbonate.

Silver cyanate is very slightly soluble in cold water, 100 c.c. at 12° dissolve 0·006 gram., but it is much more soluble in hot water. It is readily soluble in aqueous ammonia, and sparingly soluble in cold dilute nitric acid.

Sulphocyanides or **Thiocyanates.** (Ger. *Rhodanide* or *Schwefelcyanide*.)

At the present time sulphocyanides are obtained exclusively from the hydrocyanic acid of coal gas, but a modification of Gélis' synthetic process was working in 1907.

A. W. Hofmann (Reports by the Juries, Inter. Exhib. of 1862, 59–63), said that at that time ammonium sulphocyanide obtained by washing the spent oxide of gasworks was only treated to recover its ammonia, the sulphocyanide being thrown away. In 1863 P. Spence (Eng. Pat. 2364 of 1863 (provisional only)) proposed to separate the sulphocyanides in gas liquor (after distilling off the ammonia) in the form of cuprous sulphocyanide by adding copper and ferrous sulphates, and the idea has been revived in various forms since that time, but it does not appear to have become of any importance. Gas liquor is really a very dilute solution of sulphocyanide, as the following figures, calculated from Linder's analyses of various English gas liquors (Chief Inspector of Alkali Works, 42nd Rep. 1905, 35), show :—

	Grams per litre				
	1	2	3	4	5
HCN as ferrocyanide	0·068	0	0·576	0·460	0
HCN as sulphocyanide	1·688	4·457	1·238	1·029	1·042
HCN as hydrocyanic acid	0·680	0	0·030	0·050	0·355

These liquors had all been stored for some time : perfectly fresh gas liquor contains ammonium sulphide and cyanide. By the action of the air, the former is oxidised to ammonium polysulphide, which convert the cyanide into sulphocyanide ; thus :

$$(NH_4)_2S_2 + NH_4CN = NH_4SCN + (NH_4)_2S$$
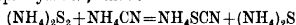
The recovery of the whole of the hydrocyanic acid of coal gas in the form of a concentrated solution of ammonium sulphocyanide is possible by applying this reaction in a suitable way.

A very large part of the gas liquor produced is distilled and the gases evolved, consisting of ammonia, carbon dioxide, sulphuretted hydrogen, and a little hydrocyanic acid, passed into sulphuric acid for the production of ammonium sulphate. The unabsorbed gases, mixed with steam, are first cooled, which yields an aqueous solution of hydrocyanic acid and sulphuretted hydrogen, known as ' Devil liquor,' which is run to waste.

The cooled gases are passed usually into a heap of ferric hydroxide, in order to absorb the sulphuretted hydrogen, or occasionally they are burned in a Claus kiln, in which, as Carpenter has shown, the hydrocyanic acid is converted by steam into ammonia.

The waste liquors from the ammonia stills contain relatively considerable quantities of calcium sulphocyanide (about 0·15 p.c. SCN) and phenols, and are usually discharged into sewers. Frankland and Silvester (J. Soc. Chem. Ind. 1907, 231), and Fowler, Ardern and Lockett (*ibid.* 1911, 174), have published detailed accounts of the bacterial oxidation of these impurities in the septic tank system of sewage treatment. It appears that sulphocyanides are practically completely oxidised in the contact beds, if sufficient time is allowed. Fowler and Holton (J. Soc. Chem. Ind. 1911, 180) have shown that 92–98 p.c. of the impurities in the ammonia still effluent can be oxidised by allowing it,

after dilution to one-tenth of its original strength, to trickle through a column of clinker inoculated with bacterial material from a contact bed of a sewage work; one cubic yard of filter is required for 10 galls. per day of effluent.

Synthesis of sulphocyanides from ammonia and carbon disulphide.—In Gélis' original process (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63; A. Gélis, Eng. Pat. 1816 of 1860), a concentrated solution of ammonia and ammonium sulphide was agitated with carbon disulphide, yielding a solution of ammonium sulphocarbonate

$$(NH_4)_2S + CS_2 = (NH_4)_2CS_3$$
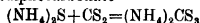
which was then heated to 90°–100° with potassium sulphide

$$2(NH_4)_2CS_3 + K_2S = 2KCNS + _2NH_4HS + 3H_2S$$

A very large amount of sulphuretted hydrogen is produced in this way, the disposal of which would occasion much trouble and expense. Gunsburg and Tchernkiac (Eng. Pat. 1148 of 1878; 1359 of 1879; 1261 of 1881) heated a 20 p.c. solution of ammonia with carbon disulphide in autoclaves provided with stirrers at 100° until a pressure of 15 atmos. was reached, which indicated the end of the reaction. As Conroy (J. Soc. Chem. Ind. 1896, 15, 8) has shown, ammonium sulphocyanide is formed quantitatively under these conditions, the large pressure developed being due to the formation of the volatile ammonium sulphide $4NH_3 + CS_2 = NH_4SCN + (NH_4)_2S$.

Subsequent improvements were all in the direction of diminishing the quantity of ammonia required and reducing the pressure in the autoclaves. The simplest and most effective way of doing this is to add lime to the charge (Crowther and Rossiter, Eng. Pat. 17846 of 1893; Brock, Hetherington, Hurter, and Raschen, Eng. Pat. 21451 of 1893), the reaction then taking place in accordance with the equation:

$$2NH_3 + 2CS_2 + 2Ca(OH)_2 = Ca(SCN)_2 + Ca(SH)_2 + 4H_2O$$
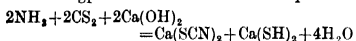
A certain excess of ammonia over the quantity required by the equation must be used to prevent the formation of calcium sulphocarbonate. The excess of ammonia is distilled off, the residual mixture treated with carbon dioxide to remove sulphuretted hydrogen (in this way used in the treatment of Leblanc alkali waste), and the calcium carbonate filtered off. The clear solution of calcium sulphocyanide is easily converted into other salts.

THE PRINCIPAL SULPHOCYANIDES.

Potassium sulphocyanide KSCN crystallises in anhydrous, striated prisms or needles of sp.gr. 1·9, which melt at 172·3°. It resembles salt-petre in appearance and taste. It is deliquescent and very soluble in water, 100 grams of which dissolve 177·2 grams at 0°, 217 grams at 20°, and 239 grams at 25°. It is also soluble in anhydrous ammonia and in many organic liquids. The solubilities (in grams per 100 grams of solvent) are :

Acetone, 20·8 at 22°; 20·4 at 58°.

Ethyl acetate, 0·44 at 0°; 0·4 at 14°; 0·2 at 79°.

Amyl alcohol, 0·18 at 13°; 2·14 at 100°.

Pyridine, 6·75 at 0°; 4·97 at 58°, and 3·21 at 115°.

The fused salt becomes deep blue at 430°; the colour is said to be due to the liberation of sulphur. The sulphocyanides are plant poisons. Frankland and Silvester found that gold-fish were not affected in 24 hours by quantities of potassium sulphocyanide up to 260 parts SCN per 100,000 of water, but even as little as 10 parts of SCN per 100,000 is sufficient to stop the multiplication of, and eventually to kill, *Bacillus coli communis*.

Ammonium sulphocyanide NH₄SCN crystallises in anhydrous, colourless leaflets of sp.gr. 1·3, which melt at 159°; 100 grams of water dissolve 122 grams at 0° and 162 grams at 20°; it is readily soluble in alcohol. When heated a little above its melting-point, it is partly converted into the isomeric thiourea. At 220° decomposition takes place, ammonia, sulphuretted hydrogen, and carbon disulphide being evolved, and guanidine sulphocyanide remaining behind.

Thiocyanogen is obtained by the action of, a solution of a halogen in an anhydrous solvent on a suitable thiocyanate; a dry ethereal solution of bromine cooled to 0° and lead thiocyanate give good results. By cooling an approximately N/2-solution in carbon disulphide to −70° thiocyanogen is obtained in almost colourless crystals, melting at −3° to −2°, and decomposing at the ordinary temperature. In its chemical behaviour thiocyanogen resembles the halogens; it is at least as strongly electro-negative as iodine. The molecular weight has not yet been determined, but the constitution of thiocyanogen is probably CN—S—S—CN (E. Söderbäck, Annalen, 1919, 419, 217).

ANALYSIS OF CYANIDES.

The methods of analysis described here are those commonly employed in technical laboratories.

Detection of hydrocyanic acid.—The material is distilled with an acid and the distillate examined. The Prussian blue test may be applied by evaporating the solution (after the addition of a little sodium hydroxide) *in vacuo* at temperature below 70°, to 1 c.c.; 0·2 c.c. of 3 p.c. FeSO₄ and 0·05 gram KF are added, and, after 10 minutes, a small excess of 30 p.c. HNO₃. The blue colour is compared with that produced by a known quantity of KCN under similar conditions (A. Viehoever and C. O. Johns, J. Amer. Chem. Soc. 1915, 37, 601). The sulphocyanate test is also characteristic; the distillate containing 0·1–8 milligrams HCN is made alkaline with KOH, treated with 1 c.c. ammonium polysulphide solution and evaporated to dryness. The residue is extracted with acetone, which dissolves KSCN only. After removing the acetone by evaporation the residue is treated with 2 c.c. of 0·5 p.c. FeCl₃, and the colour matched by means of a standard sulphocyanide solution (M. O. Johnson, J. Amer. Chem. Soc. 1916, 38, 1230). Ferric sulphocyanate may be extracted from the aqueous solution by ether; meconic acid gives a similar colouration in ether, which, however, is not destroyed by 10 p.c. AuCl₃ (P. Lavialle and L. Varenne, J. Pharm. Chim. 1915, 12, 74).

Other sensitive colour tests have the disadvantage that they may be produced by

substances other than HCN. An alkaline solution of picric acid yields a reddish-violet colouration with NaCN, which is due to sodium isopurpurate $C_8H_2(NO_2)_2\cdot N(CN)_2\cdot ONa$, when excess of cyanide is used, but to amino-nitro-phenols when picric acid is in excess, as is usually the case (A. C. Chapman, Analyst, 1910, 35, 469). The liquid to be tested is mixed with an equal volume of a solution containing 0·05 p.c. picric acid and 0·5 p.c. Na_2CO_3, and digested at 40° for 1 hour. The colour is then compared with that produced by a standard HCN solution; 1 part of HCN in 500,000 parts water can be detected (A. D. Waller, Proc. Roy. Soc. 1910, B. 82, 574).

The cyanogen liberated by the action of HCN or a cupric salt oxidises many substances to coloured products, the tests are highly sensitive, but uncertain owing to the difficulty of excluding other oxidising agents. For details, see Thiéry (phenolphthalin), J. Pharm. Chim. 1907, 25, 51; C. Pertusi and E. Gastaldi (benzidine), Chem. Zeit. 1913, 37, 609; G. W. Anderson (guaiacum), J. Soc. Chem. Ind. 1917, 36, 195; J. Moir. and J. Gray, J. Chem. Met. and Min. Soc. S. Africa, 1910, 11, 152; and J. Moir, Chem. Soc. Proc. 1910, 26, 115 (hydrocœrulignone, tolidine, dianisidine).

Alkali cyanides. Owing to the hygroscopic nature of sodium and potassium cyanides when cold, samples, taken from different parts of a cake, should be transferred at once and without touching them with the hands to a hot iron mortar, broken up coarsely, and transferred to a hot perfectly dry bottle. If the sample has to be kept for any length of time before it is analysed, it is preferable to use glass-stoppered bottles and to grease the stopper with a little vaseline. Errors due to absorption of moisture in sampling are more common and more serious than those due to inaccuracies in testing.

Estimation of cyanogen.—5 grams of the sample are weighed out and made up to 500 c.c.; 25 c.c. of the solution are diluted to 200–300 c.c. and titrated with a solution of pure silver nitrate until the faintest visible turbidity results. The silver nitrate must be neutral and free from lead and zinc especially. A convenient strength of solution is obtained by dissolving 13·1 grams of silver nitrate in 1 litre of distilled water: 1 c.c. of this solution is equivalent to 0·01 gram of KCN. The solution is standardised by means of a solution of pure sodium chloride (dried by heating to redness before weighing) containing 4·487 grams per litre; 1 c.c. of the silver solution should exactly precipitate 1 c.c. of the sodium chloride solution using pure potassium chromate as indicator. In impure solutions of cyanides, the end point is often more easily observed if a little caustic soda (or a few drops of ammonia) and a crystal of potassium iodide are added before running in the silver nitrate solution. Sulphides interfere with the test, but they are easily removed by shaking the solution with a little lead carbonate and filtering it.

Estimation of sulphide.—10 grams of the finely powdered sample are dissolved in 15 c.c. of ordinary water and a solution of lead nitrate (2·4 grams per litre) run in gradually. The mixture is stirred until the colloidal lead sulphide at first formed has coagulated into brown flocks;

a drop of the solution is then placed on blotting paper beside a drop of the lead nitrate solution, and the two allowed to run together. When no difference can be detected between the colour of the paper where the drops have mixed and where they have not, the titration is considered to be at an end; 1 c.c. of the lead solution=0·001 gram of K_2S (T. Ewan, J. Soc. Chem. Ind. 28, 10, 1909; Rossiter, *ibid.* 30, 583, 1911).

Water is estimated by weighing out about 1 gram of the coarsely powdered sample into a small distilling flask (10–20 c.c.) which is then evacuated by a good water pump or preferably by a mercury pump. The sample is then warmed, gently at first, and finally to 200°–300°. The whole of the moisture is expelled in a few minutes without appreciable decomposition of the cyanide.

Carbonate is conveniently estimated by precipitating a suitable portion of the solution with barium chloride in the cold (to avoid decomposition of cyanate). The precipitate is washed and titrated, together with the paper, with normal hydrochloric acid and methyl orange.

Chloride. The solution is neutralised with dilute nitric acid, and methyl orange and boiled for about 1 hour (in a draught cupboard, of course) to drive off the hydrocyanic acid and decompose cyanate. The chloride remaining (Richards and Singer, Amer. Chem. J. 27, 205, 1902) is then precipitated by a known excess of standard silver nitrate solution, the silver chloride filtered off and the excess of silver titrated with ammonium sulphocyanide and iron alum in the usual way.

If ferrocyanide is present, it may be precipitated with excess of silver nitrate in ammoniacal solution; by acidifying the filtrate with nitric acid, silver chloride is precipitated and may be weighed.

Cyanamide in presence of alkali cyanides is easily estimated by exactly neutralising the solution of 1 gram of the substance in 100 to 150 c.c. of water with *nitric acid*, and then boiling for 20 minutes to expel hydrocyanic acid. After cooling, 2 or 3 drops of ammonia are added, and then excess of silver nitrate. The canary-yellow precipitate of silver cyanamide Ag_2CN_2 is filtered off and dissolved in cold dilute nitric acid (which usually leaves a small residue of undissolved silver cyanide). The silver in the solution is then titrated by means of ammonium sulphocyanide, using ferric alum as indicator. The method is applicable to most substances containing cyanamide, the boiling with acid being, of course, omitted when little or no cyanide is present.

When cyanamide is the principal constituent this method is insufficiently accurate, because the composition of the precipitate is not exactly that required by the formula Ag_2CN_2, the silver content depending to a small extent on the excess of silver nitrate used in precipitation. Caro (Zeitsch. angew. Chem. 1910, 23, 2405) has shown, however, that it contains the whole of the cyanamide nitrogen, which is very readily estimated by Kjeldahl's method.

Cyanate. The solution is acidified with nitric acid and boiled for 20 minutes at least to expel hydrocyanic acid, and convert the cyanate into ammonium nitrate and carbon dioxide.

The ammonia is then distilled off, after adding excess of caustic soda, and estimated by titration with N-hydrochloric acid as usual. In presence of cyanamide, the method is not available, because some ammonia is formed from the cyanamide when it is boiled with caustic soda. In this (rather uncommon) case, the cyanate must be estimated by collecting the carbon dioxide evolved when the sample is boiled with acid (Ewan, J. Soc. Chem. Ind. 1904, 23, 244).

Ferrocyanide is most conveniently estimated, either alone or in presence of cyanides, by titration with a standard solution of zinc sulphate until a drop of the solution no longer gives a blue colour when brought in contact with a drop of ferric solution on paper. A zinc alkali ferrocyanide of somewhat variable composition is precipitated, and H. G. Colman (Analyst, 33, 261, 1908 ; and J. Soc. Chem. Ind. 27, 806, 1908) has shown that the quantity of zinc solution required to precipitate a given quantity of ferrocyanide depends, to some extent, on the nature of the metal in the ferrocyanide used. This effect can be eliminated almost entirely by adding an excess of potassium sulphate. The method is carried out as follows : a solution containing 10.2 grams of $ZnSO_4, 7H_2O$ and 10 c.c. of concentrated sulphuric acid per litre is standardised against pure potassium ferrocyanide ; 25 c.c. of a solution containing 10 grams of $K_4Fe(CN)_6 \cdot 3H_2O$ per litre, mixed with 25 c.c. of a saturated solution of potassium sulphate, 25 c.c. of water, and 10 c.c. of 1 : 10 sulphuric acid, are convenient quantities. Equal volumes of the standard zinc and ferrocyanide solutions are required, the precipitate formed having the composition $Zn_3K_2(FeCy_6)_2$ (R. Meurice, Ann Chim. anal. 1913, 18, 342). Subsequent titrations should be made as nearly as possible under the same conditions.

A more accurate method is that of W. Feld (Journ. für Gasbeleuchtung, 47, 565, 1903). Ferrocyanide, equivalent to 0.3 to 0.5 gram of yellow prussiate is boiled for 5 minutes with 10 c.c. of N-NaOH and 15 c.c. of 3 (molecular) N-HgCl$_2$. If cyanide is present, the boiling is continued for 10 minutes and the hydrocyanic acid distilled into caustic soda and titrated with silver nitrate with potassium iodide as indicator. 100 c.c. of boiling $0.1N$-HgCl$_2$ are now run in, and the boiling continued for 10 minutes to convert ferrocyanide into mercuric cyanide This is then distilled with 30 c.c. of $3N$-sulphuric acid for 20–30 minutes, and the hydrocyanic acid collected in caustic soda and titrated as before. The conversion of the ferrocyanide into mercuric cyanide is avoided by H. E. Williams' procedure (J. Soc. Chem. Ind. 1912, 31, 468). After distilling off hydrocyanic acid in the way just described (lead nitrate may be used instead of magnesium chloride), 0.05–0.1 gram of pure cuprous chloride dissolved in HCl is added, and the hydrocyanic acid distilled off by $\frac{1}{2}$ hour gentle boiling. Even insoluble ferrocyanides are completely decomposed.

The estimation of the valuable constituents of gasworks products (cyanide and ferrocyanide) is performed by triturating 30 to 40 grams of the material in a mortar with excess of a cold solution of caustic soda for several hours. A little ferrous sulphate may be added to convert cyanide into ferrocyanide. The filtrate is treated with 4 to 5 times its volume of methylated spirit. Carbonyl ferrocyanide (from 2 to 5 p.c. of the cyanogen is usually present in this form, but exceptionally as much as 20 p.c. may be present), sulphocyanide, sulphide, and excess of caustic soda remain in solution, whilst the whole of the sodium ferrocyanide is precipitated. The precipitate is then treated by one of the methods described above (H. G. Colman, Analyst, 33, 261, 1908 ; and J. Soc. Chem. Ind. 27, 806, 1908 ; F. W. Skirrow, *ibid.* 29, 319, 1910).

Sulphocyanide. Ferrocyanide, if present, is first removed from the solution by adding iron alum after acidifying slightly. The filtrate is treated with acid sodium sulphite in excess and then with copper sulphate and boiled for 1 or 2 minutes. The precipitate of cuprous sulphocyanide, which may be mixed with copper sulphide, is filtered off and washed with boiling water. It is then digested with excess of caustic soda which gives cuprous hydroxide and a solution of sodium sulphocyanide. This is separated by filtration, acidified with nitric acid, and titrated with silver nitrate, using a ferric salt as indicator (Linder, 43rd Alkali Report, 1906, 39).

The small quantities of cyanogen compounds in concentrated ammonia liquor may be estimated by converting them into ferric sulphocyanide-and measuring the depth of colour by means of the tintometer (P. E. Spielmann and H. Wood, J. Soc. Chem. Ind. 1919, 38, 43T, and 369T). Sulphocyanide is first estimated by acidifying the diluted sample, in the cold, with sulphuric acid, and removing ferrocyanide by means of a small excess of iron alum ; a large excess of iron alum is added to the filtrate and the depth of colour measured. Cyanide is converted into sulphocyanide by digestion at 30°–35° with ammonium polysulphide, and a second estimation made as above described. Thiocarbonate is converted into sulphocyanide by digestion at 70°–75° for 45 minutes, cyanide and ferrocyanide remaining unaffected.

Alkali metals in commercial cyanides. 1 gram of the substance is evaporated to dryness with excess of hydrochloric acid. Traces of iron and calcium are removed by re-dissolving, adding a drop of ammonium carbonate, and filtering. The solution is again evaporated to dryness, and the residue is gently fused and weighed. The mixture of alkaline chlorides is dissolved in water and an aliquot portion titrated with silver nitrate, using chromate as indicator. If n gram of cyanide has yielded a gram of the pure mixed chlorides containing b gram of chlorine, the percentage of potassium in the cyanide is given by the formula

$$\left(\frac{2.431a - 4.012b}{n}\right)100$$

This method is sufficiently accurate for most purposes, but the gravimetric estimation of the potassium as potassium platinichloride must be resorted to if a greater degree of accuracy is required.　　　　　　　　　　　　　　T. E.

CYANIDIN, CYANIN v. ANTHOCYANINS.

CYANINE and **CYANINE DYESTUFFS** v. QUINOLINE COLOURING MATTERS.

CYANITE v. KYANITE. ●

**CYANOMACLURIN.** $C_{13}H_{12}O_6$, a colourless

compound existing in Jakwood is closely allied to the catechins, and may possibly belong to the same group. In its general reactions, indeed, it is very similar to these compounds, but differs from them in that by alkali fusion it yields β-resorcylic acid and not protocatechuic acid.

A full description of the properties of this compound is given in the article on JAKWOOD.

CYANOSINE v. TRIPHENYLMETHANE COLOUR-ING MATTERS.

Iso-CYANURIC ACID v. FULMINURIC ACID.

CYCLOFORM. The trade name of *iso*butyl ester of *p*-amino benzoic acid

$$NH_2 \cdot C_6H_4 \cdot COOC_4H_9$$
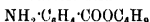
used as a local anæsthetic. A white crystalline powder, m.p. 65°. Sparingly soluble in water (0·022 p.c.), readily soluble in alcohol and ether.

CYLINDRITE. (*Kylindrit*, Ger.) A complex sulphide ore of tin, $Pb_3FeSn_4Sb_2S_{14}$, containing, according to this formula, Sn 25·85 p.c. It forms very peculiar cylindrical rolls of thin folia, the concentric shells parallel to the axis of the cylinder readily separating under pressure. The smooth, bright surfaces of separation no doubt represent the cleavages of cylindrically curved crystals. The colour is blackish lead-grey, with a brilliant metallic lustre. The mineral marks paper, and is difficult to pulverise, in these respects resembling graphite. The ore consists of numbers of these rolls, which measure up to 3 cm. in length and 1 cm. in diameter, confusedly aggregated together, or sometimes with a sub-parallel grouping, the interspaces being filled with massive material. It has been found in some quantity in the Santa Cruz mine, at Poopó, Bolivia. The above formula, written in the form
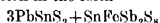
$$3PbSnS_2 + SnFeSb_2S_8$$

brings out a relation between cylindrite and the allied Bolivian minerals, teallite ($PbSnS_2$) and franckeite ($3PbSnS_2 + Pb_2FeSb_2S_8$). Analyses I and II by G. T. Prior (1904), III. by A. Frenzel (1893):

		I	II	III
Pb	.	35·24	34·58	35·41
Fe	.	2·81	2·77	3·00
Ag	.	0·50	0·28	0·62
Sn	.	25·65	25·10	26·37
Sb	.	12·31	12·98	8·73
S	.	23·83	23·88	·24·50
		100·34	99·59	98·63
Sp.gr.	.	5·46	5·49	5·42

L. J. S.

CYMARIN. The physiologically active constituent of the root of *Apocynum cannabinum* and *A. androsœmifolium*, is a glucoside, $C_{30}H_{46}O_{10}$, colourless glistening prisms, m.p. 135°-140°, which, when boiled with alcohol containing hydrochloric acid, is resolved into *cymarose* $C_7H_{14}O_4$, colourless prisms, m.p. 88°, a substance resembling digitoxose, of which it is probably a methyl ether, and *cymarigenin* $C_{23}H_{30}O_5$, a lactone which appears to be identical with apocynamarin (Moore, Chem. Soc. Trans. 1909, 95, 734); it crystallises from aqueous methyl alcohol in rhombic tablets, m.p. 171° (decomp.). With a solution of a diazonium salt, cymarigenin forms dyes; it reduces ammoniacal silver nitrate, forms a

benzoyl derivative $C_{36}H_{36}O_7$,$\frac{1}{2}H_2O$, pearly leaflets, m.p. 230°, and when treated with hydrogen chloride in chloroform solution, is converted into *anhydro cymarigenin* $C_{23}H_{28}O_4$, rosettes of crystals, m.p. 246° (decomp.). (Windaus and Hermanns, Ber. 1915, 48, 979).

According to Impens (Pflüger's Archiv. 1913, 153, 239), cymarin is not a glucoside. It corresponds in activity with digitalis, being slightly more potent as a diuretic and slightly less so as a cardiac stimulant. The 'cynotoxin' of Finnemore and 'apocynamarin' are probably decomposition products of cymarine. V. DIGITALIS and STROPHANTHUS.

CYMENES. *Cymols.* The name *cymene* was first applied to the hydrocarbon isolated by Gerhardt and Cahours (Ann. Chim. Phys. [3] 1, 102 and 372) from Roman oil of cumin, which is the ethereal oil of *Cuminum cyminum*. Until 1891 this hydrocarbon was wrongly called *p*-methylpropylbenzene, but in that year Widman (Ber. 1891, 439, 970, 1632) proved it to be the *iso*propyl- compound (*see also* Fileti, J. pr. Chem. [2] 44, 150). Frequently, however, the various benzene hydrocarbons of the formula $C_{10}H_{14}$ are grouped together under the collective name of *cymenes*. No fewer than 22 of these are theoretically possible, of which 18 have been prepared; but only the most important, namely, cymene proper (*p*-methyl*iso*propyl-benzene) and the tetramethylbenzenes are described here.

p-**Methyl*iso*propylbenzene** (*Cymene*)

$$`CH_3)_2CH \cdot C_6H_4 \cdot CH_3 \ (1, 4)$$
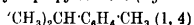
occurs in Roman oil of cumin (Gerhardt and Cahours, *l.c.*; Brühl, Ber. 1892, 149; Wolpian, Chem. Soc. Abstr. 1897, i. 357); in the volatile oil from the seeds of the water-hemlock (*Cicuta virosa*) (Trapp, Annalen, 108, 386); in the oil from *Ptychotis ajowan* (H. Müller, Ber. 2, 130); in oil of thyme (Lallemand, Annalen, 102, 119; Labbé, Bull. Soc. chim. 1898, [iii.] 1009) along with thymol $C_{10}H_{14}O$ and thymene $C_{10}H_{16}$; in eucalyptus oil (from *Eucalyptus Globulus*) (Faust and Homeyer, Ber. 7, 1429); in oil of caraway (Wolpian, Chem. Soc. Abstr. 1897, i. 17); in bitter fennel oil (Tardy, J. Pharm. Chim. 1897, 98); in oil of lemon grass (Barbier and Bouveault, Compt. rend, 121, 1159; Stiehl, J. pr. Chem. 1898, 51); in oil of origanum (Gildermeister, Arch. Pharm. 1895, 174); in geraniol (Semmler, Ber. 1891, 205); and in American petroleum (Mabery, Amer. Chem. J. 19, 419). Considerable quantities of crude cymene, known as sulphide turpentine, collect on the surface of the liquid in the separator used in recovering sulphur dioxide in the manufacture of wood pulp. May be obtained from camphor by abstracting from it the elements of water

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O$$
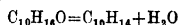
by heating it either with phosphorus pentoxide (Dumas, Ann. Chim. Phys. 50, 226; Delalande, *ibid.* [3] 1, 368) or with phosphorus pentasulphide (Pott, Ber. 2, 121), or with phosphorus pentachloride (Lippmann and Louguinine, Bull. Soc. chim. [2] 7, 374; *see also* Brühl, *l.c.*; Tiemann, Ber. 1895, 1089). Various isomerides of camphor yield cymene by the same treatment. The terpenes $C_{10}H_{16}$ may be converted into cymene by withdrawing two atoms of hydrogen; this

may be effected in the case of oil of turpentine, for example, by distilling it with bromine (Oppenheim, Ber. 5, 94 and 628), or better, with iodine (Kekulé, *ibid.* 6, 437). Old turpentine generally contains cymene (Wallach, Chem. Zentr. 1898, i. 572; Kondakow and Schindelmeier, Chem. Zeit. 30, 722). It has been obtained synthetically from *p*-brom*iso*propylbenzene by means of methyl iodide and sodium (Widman, *l.c.*). To prepare cymene, camphor is warmed with an equal weight of phosphorus pentoxide, the cymene is poured off, treated again twice with a little phosphorus pentoxide, and finally rectified from sodium. The yield varies from 50 to 80 p.c. (Fittica, Annalen, 172, 307). It can also be prepared from *iso*propyliodide, and *p*-bromotoluene (Reuter, Chem. Zentr. 1892, i. 625; Brühl, *l.c.*) or from *iso*propylchloride, toluene and aluminium chloride (Silva, Bull. Soc. chim. [n.] 43, 321).— Liquid boiling at 177°-177·5° (corr.); sp.gr. 0·8670 at 7·9°/4° (Perkin, Chem. Soc. Trans. 1896, 1125; 1900, 267). With chromic acid it yields paratoluic acid ((CH₃·C₆H₄·CO₂H) and terephthalic acid C₆H₄(CO₂H)₂ (1, 4); with potassium permanganate, hydroxy*iso*propylbenzoic acid (CH₃)₂(OH)C₆H₄·CO₂H (1, 4). Taken internally, it appears in the urine as cumic (*p-iso*propylbenzoic) acid

$$(CH_3)_2CH·C_6H_4·CO_2H \ (1, 4)$$
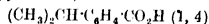
The preparation of cumene (*q.v.*) from propyl-bromide, benzene, and aluminium chloride, and that of cymene from *p*-bromotoluene, normal propylbromide, and sodium (Fittig, Schafer, and König, Annalen, 149, 331) was for a long time the cause of great confusion in ascertaining the constitution of members of the cumene and cymene groups, as it was not realised that in each case the propyl- group changed into the *iso*propyl- group owing to the temperature of the reaction not being regulated.

Tetramethylbenzenes :

1. *Consecutive tetramethylbenzene* (*Prehnitene*) C₆H₂(CH₃)₄ (1, 2, 3, 4). When sodium durene-sulphonate

$$C_6H(CH_3)_4SO_3Na(CH_3\text{- groups } 1, 2, 4, 5 \ v. \ infra)$$

is dissolved in concentrated sulphuric acid and allowed to stand for 12 hours, prehnitene-sulphonic acid is formed. The mixture is diluted with water, saturated with barium carbonate, the barium salts converted into sodium salts, and these, by treatment with phosphorus pentachloride and ammonia, transformed first into sulphonic chlorides and then into sulphonamides. Prehnitenesulphonamide is separated by means of its sparing solubility in alcohol, and is then hydrolysed by heating with concentrated hydrochloric acid to 170°, when it yields prehnitene (Jacobsen, Ber. 19, 1213; *see also* V. Meyer and Molz, Ber. 1897, 30, 1278). Also obtained by heating bromocumene

$$C_6H_2Br(CH_3)(CH_3,Br,CH_3,CH_3 : 1, 2, 3, 4)$$
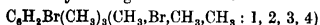
with methyl iodide, benzene, and sodium, in a sealed tube at 150° for 12 hours.—Liquid boiling at 204° (corr.); solidifies in a freezing mixture, and melts at −4°. Dilute nitric acid oxidises it to prehnitylic acid C₆H₂(CH₃)₃CO₂H.

2. *Unsymmetrical tetramethylbenzene* (*Isodurene*) C₆H₂(CH₃)₄ (1, 2, 3, 5). From bromomesitylene (*v* CUMENES), methyl iodide and

sodium in presence of benzene (Jannasch, Ber. 8, 356). Best by passing methyl chloride into a mixture of mesitylene and aluminium chloride :

$$C_6H_3(CH_3)_3 + CH_3Cl = C_6H_2(CH_3)_4 + HCl$$
$$(1, 3 \ 5) \qquad\qquad\qquad (1, 2, 3, 5)$$
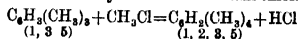
(Jacobsen, Ber. 14, 2629).—Liquid boiling at 195°-197°; solidifies in a freezing mixture. With dilute nitric acid it yields α-*iso*durylic acid, β-*iso*durylic acid, and mesitylenecarboxylic acid, isomeric acids of the formula

$$C_6H_2(CH_3)_3CO_2H$$
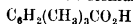
and dimethyl*iso*phthalic and dimethyltere-phthalic acids, isomeric acids of the formula C₆H₂(CH₃)₂(CO₂H)₂ (Jannasch and Weiler, Ber. 1894, 3441; 1895, 531); potassium permanganate ultimately converts it into mellophanic acid C₆H₂(CO₂H)₄ (1, 2, 3, 5).

Symmetrical tetramethylbenzene (*Durene*) C₆H₂(CH₃)₄ (1, 2, 4, 5). Occurs in coal tar (Schulze, Ber. 18, 3032). By the action of sodium on a mixture of bromopseudocumene- C₆H₂(CH₃)₃Br (1, 2, 4, 5), methyl iodide and sodium (Jannasch and Fittig, Zeitsch. Chem. 1870, 161) From toluene and methyl chloride in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys. [6] 1, 461). From o- or p-xylene, methyl chloride and aluminium chloride (Jacobsen, Ber. 14, 2629). From pseudocumene, methyl iodide, and aluminium chloride (Rugheimer and Hankel, *ibid.* 1896, 2173) —Crystalline mass, smelling like camphor? melts at 79°-80°, and boils at 189°-191° (Jacobsen). Yields by oxidation with potassium permanganate, finally pyromellitic acid

$$C_6H_2(CO_2H)_4 \ (1, 2, 4, 5)$$
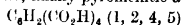
CYMOLS *v.* CYMENES.

CYMOPHENOL *v.* CAMPHORS.

CYPRIAN VITRIOL. *Copper sulphate (v.* COPPER).

CYPRIDOL. Trade name for a suspension of mercuric iodide in sterilised oil.

CYRTOLITE *v.* ZIRCON.

CYSTAMINE, CYSTOGEN. Syns. for hexamethylenetetramine.

CYSTAZOL. An additive compound of hexamethylenetetramine and sodium benzoate. Used as a urinary antiseptic.

CYSTINE, β-*disulphido-α-aminopropionic acid*

$$HO_2C·CH(NH_2)·CH_2·S·S·CH_2·CH(NH_2)·CO_2H$$

first discovered by Wollaston in a urinary calculus (Phil. Trans. 1810, 223); is a product of protein metabolism under certain pathological conditions (Blum, Beitr. chem. Physiol. Path. 1903, 5, 1; Wolf and Shaffer, Amer. J. Physiol. 19; Loebisch, Annalen, 182, 231; Niemann, *ibid.* 187, 101; Thiele, Trans. Path. Soc. 1907, 58, 255), which, according to Abderhalden (Zeitsch. physiol. Chem. 1903, 38, 557), are hereditary. Dreschel found cystine as a normal product of metabolism in the liver of horse (Arch. Anat. Physiol. 1891, 243) and porpoise (Zeit. Biol. 1896, 33, 85). It was found by Külz (*ibid.* 1890, 27, 415) among the soluble products of an artificial pancreatic digestion of fibrin; and is a constant product of hydrolysis of keratin (Mörner, Zeitsch. physiol. Chem. 1899, 28, 595): Buchtala (*ibid.* 1907, 52, 474) obtained the following percentages of cystine from the materials mentioned : human hair, 13-14·5; human nails, 5·15; horsehair, 7·98;

horse's hoofs, 3·20 ; ox hair, 7·27 ; hoofs of oxen, 5·37 ; pigs' bristles, 7·22 ; pigs' hoofs, 2·17.

According to Folin (J. Biol. Chem. 1910, 8, 9), cystine is most readily prepared from wool by boiling it in a reflux apparatus for 5–6 hours with twice its weight of strong hydrochloric acid, or until it ceases to give the biuret reaction ; on removing the free hydrochloric acid by the addition of solid sodium acetate, a dark heavy precipitate of cystine is obtained ; this is purified by decolourising a solution in 3–5 p.c. hydrochloric acid with bone-black, and precipitating the cystine in the hot filtrate by hot concentrated sodium acetate solution (*see also* Denis, J. Biol. Chem. 1911, 9, 365).

The cystine of urinary calculus is identical with that obtained from protein hydrolysis (Rothera, J. Physiol 1905, 32, 175 ; Alsberg and Folin, Amer. J. Physiol. 1905, 14, 54 ; Fischer and Suzuki, Zeitsch. physiol. Chem. 1905, 45, 405), and was proved to be β-*disulphido-α-amino-propionic acid* by Friedmann (Beitr. Chem. Physiol. Path. 1902, 2, 433). This view of its constitution was confirmed by the synthesis of racemic cystine from ethyl monobenzoylserine, obtained by reducing ethyl formylhippurate, the product of the condensation of ethyl formate and ethyl hippurate. On heating ethyl mono-benzoylserine with phosphorus pentasulphide, and hydrolysing the product, cystein is obtained, and this is readily converted into cystine by oxidation with air in an ammoniacal solution :

H·CO₂Et + NHBz·CH₂·CO₂Et
  →CHO·CH(NHBz)·CO₂Et
  →OH·CH₂·CH(NHBz)CO₂Et
  →SH·CH₂·CH(NHBz)·CO₂Et
  →SH·CH₂·CH(NH₂)·CO₂H
  →CO₂H·CH(NH₂)·CH₂·S·S·CH₂·CH(NH₂)·CO₂H
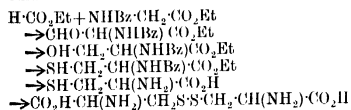
(Erlenmeyer, Ber. 1903, 36, 2720). Fischer and Raske (*ibid.* 1908, 41, 893) also obtained *r*-cystine from *dl*-α-amino-β-chloropropionic acid hydrochloride by heating it with barium hydrosulphide at 100° in sealed tubes, and oxidising the product by atmospheric oxygen in the presence of ammonia. From the natural *l*-serine the authors obtained, by a similar process, an optically active cystine which is identical with the *l*-cystine obtained from natural sources. Removal of sulphur by ammonium copper solution gives *dl*-α-*aminopropionic acid*, and removal of sulphur by zinc *dl-alanine* (Mauthner, Zeitsch. physiol. Chem. 1912, 78, 30–32).

For the importance of cystine in nitrogen metabolism, *see* Abderhalden (Zeitsch. physiol. Chem. 96, 1–147 ; Ber. 1916, 49, 2449–2473), and in humin formation, Roxas (J. Biol. Chem. 1916, 27, 71–93).

Cystine crystallises in thin colourless hexagonal plates ; it has no melting-point, but decomposes slowly at 258°–261° (Neuberg and Mayer, Zeitsch. physiol. Chem. 1905, 44, 472). It is sparingly soluble in water, insoluble in alcohol or acetic acid, soluble in acids or alkalis. The heat of combustion at constant pressure is 4·137 calories (Emery and Benedict. Amer. J. Physiol. 28, 301–307). The cystine molecule contains two asymmetric carbon atoms, and *lævo*-cystine, the naturally occurring variety, has [α]_D −97·5° in ammonia, −223° in hydrochloric acid solution (Gaskell, J. Physiol. 1907, 36, 142), or −205·28°

in a hydrochloric acid solution containing 11·2 grams hydrochloric acid in 100-cm. (Mauthner, *ibid.* 29). *l*-Cystine is converted to the extent of 50 p.c. into *r*-cystine by heating with excess of hydrochloric acid of sp.gr. 1·124, at 165° for 12–15 hours ; this decomposes at the same temperature as the active isomeride, is three times as soluble in water and can be resolved into the active components by the action of *Aspergillus niger*, the *l*- compound being consumed.

Cystine is readily reduced to *cystein* (a *amino-β-thiolpropionic acid*) HS·CH₂·CH(NH₂)·CO₂H (Baumann, Zeitsch. physiol. Chem. 1882, 8, 300 ; Mauthner, Zeit. Biol. 1901, 42, 176), which can be converted by the action of bromine-water into *cysteic acid* (α-amino-β-*sulphopropionic acid*) HO₃S·CH₂·CH(NH₂)·CO₂H, and from this, by loss of carbon dioxide, *taurine* NH₂·CH₂·CH₂·SO₃H is obtained (Friedmann, Beitr. Chem. Physiol. Path. 1902, 2, 433). According to Von Bergmann (*ibid.* 1903, 4, 92), the normal taurine in the bile originates from the cystin groups contained in the ingested protein. Cystein yields cystine on oxidation, the change occurring spontaneously in alkaline solution, although the rate is increased by the addition of a mixture of ferric chloride and potassium cyanide (Mathews and Walker, J. Biol. Chem 1909, 6, 289). For the behaviour of cystine on oxidation, *see* Denis (J. Biol. Chem. 1911, 9, 373), and for its breakdown under the action of certain bacteria, *see* Bürger (Arch. Hyg. 1914, 82, 201–211, from the abstr. Amer. Chem. Soc. 1916, 10, 2911).

Slyke's reaction (Ber 1910, 43, 3170) for α-amino acids does not give absolutely quantitative results in the case of cystine.

Cystine and tyrosine can be quantitatively separated by means of absolute alcohol saturated with hydrogen chloride (Plimmer, Bio-Chem J. 1913, 7, 311–317).

When cystine is given with food, it is completely oxidised to sulphate and excreted as such (Rothera, J. Physiol. 1905, 32, 175). Baumann and Preusse (Zeitsch. physiol. Chem. 1881, 5, 309 ; Ber. 18, 258) found that when bromobenzene was administered to animals, it was excreted as *bromophenylcystein*

CO₂H·CH(NH₂)·CH₂·S·C₆H₄Br
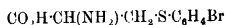
a compound crystallising in glittering needles or plates ; m.p. 180°–182°, and yielding a blue crystalline *copper salt* (C₉H₉BrSNO₂)₂Cu.

Derivatives.—Cystine forms sparingly soluble salts with *copper*, C₆H₁₀O₄N₂S₂Cu ; or *mercury*

C₆H₈O₄N₂S₂Hg₂·HgCl₂ ;
2C₆H₁₀O₄N₂S₂Hg,HgCl₂,7H₂O ;
2C₆H₈O₄N₂S₂Hg₂,Hg(NO₃)₂
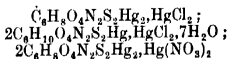
With 30 p.c. nitric or hydrochloric acid (at room temperature) it yields compounds

C₆H₁₂O₄N₂S₂·2HNO₃ and
C₆H₁₂O₄N₂S₂·2HCl
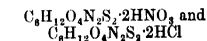
(Mörner, Zeitsch. physiol. Chem. 1914, 93, 203–208). *Benzoylcystine* C₆H₁₀O₄N₂S₂Bz₂, m.p. 156°–158°, crystallises in needles and forms a sparingly soluble sodium salt (Goldmann and Baumann, Zeitsch. physiol. Chem. 1888, 12, 254). *Cystinephenylhydantoin* is a well-defined

crystalline compound, and is used for identifying cystine. *Cystine ethyl ester hydrochloride*

$$S_2[CH_2 \cdot CH(NH_2) \cdot CO_2Et]_2, 3HCl$$
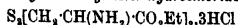
forms colourless needles, m.p. 185°, with decomposition (Friedmann, Beitr. Chem. Physiol. Path. 1902, 3, 1). Numerous *acyl*- derivatives of cystine have been described by Fischer and Suzuki (Zeitsch. physiol. Chem. 1905, 45, 405; Fischer and Gerngross, Ber. 1909, 42, 1485; Abderhalden and Wybert, Ber. 1916, 49, 2449–2473). Of these *di-l-leucyl-l-cystine* $S_2[CH_2 \cdot CH(CO_2H)NH \cdot CO \cdot CH(NH_2)C_4H_9]_2$ is a granular powder, turns yellow at 200°, and decomposes at a higher temperature, has $[\alpha]_D^{20} -136 \cdot 6°$, or, when obtained in a crystalline form, has $[\alpha]_D^{20} -141 \cdot 4°$; it gives a reddish-violet colour with copper sulphate; is precipitated by ammonium sulphate, and may be termed an *albumose*.   M. A. W.

CYSTOGEN. Syn. for hexamethylenetetramine.

CYSTOPURIN. A compound of sodium acetate and hexamethylenetetramine.

CYTISINE $C_{11}H_{14}ON_2$, prisms, m.p. 153°, b.p. 218°/2 mm., $[\alpha]_D^{17} -120°$, readily soluble in water, alcohol, or chloroform, insoluble in ether and petroleum; is a diacid base forming well-crystalline salts. It is found in the seeds of *Cytisus laburnum*, *Ulex europaeus*, *Baptisia spp.*, *Sophora spp.*, *Genista spp.*, and *Anagyris fœtida* in amounts varying from 1 to 2 p.c.

Cytisine is a secondary-tertiary base. Electrolytic reductions gives a base, tetrahydro deoxycytisine $C_{11}H_{18}N_2$. Hydriodic acid and phosphorus at 230° yields cytisoline $C_{11}H_{14}ON$, β-cytisolidine $C_{11}H_{11}N$ (this on reduction giving α cytisolidine $C_{11}H_{15}N$), hydrocarbons, and ammonia. The constitutions of α- and β-cytisolidines have been established by synthesis (Ewins, Chem. Soc. Trans. 1913, 103, 97). β-Cytisolidine is 6 : 8-dimethyl quinoline, α-cytisolidine the corresponding tetrahydro quinoline. Cytisoline, which on distillation with zinc-dust gives β-cytisolidine, is 2-hydroxy-6 : 8-dimethyl quinoline and has been synthesised

by Späth. On these grounds it has been suggested that cytisine is constituted by the fusion of three rings.

The following constitution is considered the most probable of the fourteen possibilities :—
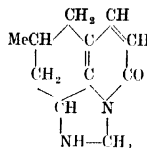
Cytisine is a violent poison. Cases of infantile poisoning from eating laburnum seeds are by no means infrequent. Dale and Lajdlaw (J. Pharm. Expt. Therap. 1912, 3, 502) have shown that the physiological action of this alkaloid is qualitatively and almost quantitatively indistinguishable from that of nicotine. *See* Späth, Monatsh. 1919, 40, 15, 93; Partheil, Ber. 1890, 23, 3201; 1891, 24, 634; Freund and Friedmann, A. 1901, ı 288; Freund, A. 1904, ı. 263; Freund and Horkheimer, A. 1906, i. 302; Freund and Gauff, Arch. Pharm. 1918, 256, 33.

Methylcytisine $C_{12}H_{16}ON_2$, prismatic needles, m.p. 137°, $[\alpha]_D -221 \cdot 6°$, readily soluble in water and organic solvents, occurs in *Caulophyllum thalictroides* (Linn.) (Power and Salway, Chem. Soc. Trans. 1913, 103, 191); it may also be obtained by methylating cytisine. The salts are crystalline.

The physiological action of the base is similar to that of cytisine (*q.v.*), but the alkaloid is less potent.

Caulophylline (Lloyd, Proc. Amer. Pharm. Assoc. 1893, 41, 115) is methyl cytisine.

Anagyrine $C_{15}H_{22}ON_2$ (?), amorphous, occurring along with cytisine in the seeds of *Anagyris fœtida*, is possibly butyl cytisine (Klostermann, Diss. Marburg, 1898; Chem. Zentr. 1899, i. 1130; Partheil and Spasski, Apoth. Zeit. 1895, 10, 903; Goessmann, Arch. Pharm. 1906, 244, 20).   A. J. E.

D.

DAGUERREOTYPE *v.* PHOTOGRAPHY.

DAHL'S ACIDS. 1-Naphthylamine-4-7- and 4.6.-disulphonic acids. *v.* NAPHTHALENE.

DAHLIA. Syn. *Hofmann's violet, Primula* (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

DAHMENITE *v.* EXPLOSIVES.

DAMASCENINE $C_{10}H_{13}O_3N$, crystalline, m.p. 25°-26°, b.p. 154°/15 mm., 270°/750 mm., occurs in the seeds of *Nigella damascena* (Linn.) (Schneider, Pharm. Centrb. 1890, 31, 173) and *N. aristata* (Keller, Arch. Pharm. 1908, 246, 1). Its constitution was established by synthesis (Ewins, Chem. Soc. Trans. 1912, 101, 544), and

shown to be methyl-2-methylamino-3-methoxy benzoate :
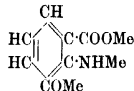
Keller's 'methyl damascenine' is identical with damascenine and 'damasceninic acid' $C_9H_{11}O_3N$, said by Pommerehne (Arch. Pharm. 1900, 238, 531) to be isomeric with damascenine, is obtained on hydrolysis of the alkaloid. Damascenine is mildly narcotic.   A. J. E.

DAMMAR RESIN, DAMMARYL, DAMMARYLIC ACID *v.* RESINS.

DANAITE *v.* **MISPICKEL.**

DANALITE. A rare sulpho-silicate mineral, with the formula $3R_3SiO_4 \cdot RS$, where R represents Fe, Zn, Be, Mn, containing BeO about 14 p.c. The flesh-red or grey cubic crystals are octahedral or tetrahedral in habit; sp.gr. 3·35–3·43; H.=5½–6. It occurs in granite at Rockport and Gloucester, in Massachusetts, and large crystals have been found in Cornwall. Closely allied is the tetrahedral-cubic mineral *helvite*, which contains about the same amount of beryllium, but with a preponderance of manganese and no zinc. L. J. S.

DANDELION ROOT. *Taraxaci radix*, B.P.; *Taraxacum*, U.S.P. (*Pissenlit*, Fr.; *Löwenzahnwurzel*, Ger.) The root of the common dandelion, *Taraxacum officinale* (Weber) (Bentl. a. Trim. 159), is used in medicine for its mild laxative and tonic properties. It is administered either in the form of expressed juice or weak spirituous extract. The roots employed should be collected in the autumn.

The latex contains two crystalline bitter principles, *taraxacin* and *taraxacerin* (Polex, Arch. Pharm. 19, 50; Kromayer, *ibid.* 105, 6) The root further contains *inulin*, 24 p.c. in October, according to Dragendorff (Sachsse's Farbstoffe, 125), but only 1·7 p.c. in March, when, however, 17 p.c. of uncrystallisable sugar and 19 p.c. of *levulin* is present. The latter carbohydrate is soluble in cold water to a sweet solution, without any action on polarised light.

The leaves and stalks, but not the root of the dandelion, contain *inosite* (Marmé, Annalen, 129, 222). G. B.

DAPHNETIN. Daphnetin is present in the form of its glucoside *daphnin* in the bark of the *Daphne alpina* (Linn.) and *D. mezereum* (Linn). The concentrated alcoholic extract is digested with boiling water, filtered, and treated with lead acetate solution. The precipitate is removed, basic lead acetate added to the filtrate, the lead compound of the glucoside decomposed with sulphuretted hydrogen, and the solution evaporated (Zwenger, Annalen, 115, 8).

Daphnin $C_{15}H_{16}O_9, 2H_2O$ crystallises in prisms, melting at 200°, and dissolves in alkaline solutions with a yellow colour. It is hydrolysed by boiling dilute acids with formation of daphnetin and glucose :

$$C_{15}H_{16}O_9 + H_2O = C_9H_6O_4 + C_6H_{12}O_6$$
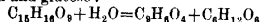
Daphnetin $C_9H_6O_4$ forms pale yellow needles, is soluble in alkalis with a yellow colour, and gives a yellow precipitate with lead acetate solution. On acetylation, a *diacetyl-* derivative $C_9H_4O_4(C_2H_3O)_2$ is obtained, and by means of ethyl iodide a *diethyl ether* $C_9H_4O_2(OEt)_2$ is produced. When daphnetin diethyl ether is boiled with caustic soda solution, the diethyl ether of *daphnetinic acid*

$$(OEt)_2C_6H_2 {\Large\langle} {{-OH}\atop{-CH=CH \cdot COOH}}$$
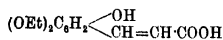
is produced in the form of its sodium salt, which when ethylated gives the *triethyl* derivative :

$$(OEt)_2C_6H_3 {\Large\langle} {{-OEt}\atop{-CH=CH \cdot COOH}}$$

By oxidising daphnetic acid triethyl ether *triethoxybenzaldehyde* is formed, which is readily converted into *triethoxybenzoic* acid. The

silver salt of this acid, when destructively distilled, gives pyrogallol triethyl ether. Daphnetin is accordingly a *dihydroxycoumarin*, and has the following constitution :—
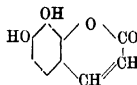
(Will and Yung, Ber. 1884, 17, 1081).

It has been synthetically prepared by heating pyrogallol with malic acid in the presence of sulphuric acid (Pechmann, Ber. 17, 933) :

$$C_4H_6O_5 + C_6H_3(OH)_3 = C_9H_6O_4 + CO_2 + 2H_2O + H_2$$
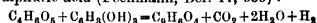
and by the condensation of pyrogallic aldehyde with sodium acetate (Gattermann and Koebner, Ber. 1899, 32, 287) :

$$C_6H_2(OH)_3 \cdot CHO + CH_3 \cdot COOH = C_9H_6O_4 + 2H_2O$$
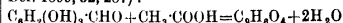
Daphnetin is a yellow colouring matter, and gives with mordanted woollen cloth the following shades :—

Chromium	*Aluminum*
Olive-yellow	Pale olive-yellow
Tin	*Iron*
Very pale yellow	Olive-black

(Perkin and Wilson, Chem. Soc Trans. 1903, 83, 134). A. G. P.

DAPICHO or **ZASPIS.** The South American name for the caoutchouc which exudes from the roots of *Hevea guianensis* (Aubl.).

DARWINITE *v.* **DOMEYKITE.**

DATE. The fruit of the date palm, *Phœnix dactylifera*. A palm of the tropics of Africa and the East Indies. It furnishes food to a large population in Egypt and Arabia.

The fruit grows in bunches of from 15 to 20 lbs. weight, and a tree usually produces about 20 bunches annually. The date palm also yields a sweet sap, which flows, when incisions are made in the trunk, almost continuously from November to March; the sap is clarified and boiled down, when a brown sugar, known as jaggery, is obtained (Bied. Zentr. 1884, 284).

Analyses of the flesh of dates give :

Water	Protein	Fat	Sol carbo-hydrates	Fibre	Ash
28·8	1·9	trace	63·1	2·7	1·6

Dried dates, according to König, have the mean composition :

Water	Protein	Fat	Sugar	Free carbo-acid hydrates	Other carbo-hydrates	Fibre	Ash
18·5	1·9	0·6	67·2	1·3	4·3	3·8	1·8

Among the 'soluble carbohydrates' is included about 3 p.c. of pentosans, while the date stone contains about 2·7 p.c. of the same substances (Wittmann, Zeitsch. landw. Versuchs. Oesterreich. 1901, 4, 131).

König gives, as the composition of the date stone :

Water	Protein	Fat	free extract	Nitrogen carbo-hydrates	Fibre	Ash
7·7	5·2	9·0	53·0		24·0	1·1

Dates are sometimes used as coffee substitutes, the whole fruit being occasionally employed, but more usually the stones only.

König gives as the composition of 'date-coffee' :

Water	Protein	Fat	Sugar	Other carbo-hydrates	Fibre	Ash
6 6	5·5	7·9	2·2	48·7	27·8	1·3

yielding about 14 p.c. of its weight to water. H I.

DATHOLITE v. DATOLITE.

DATISCA CANNABINA (Linn.). This is a tall, erect herb, resembling hemp, belonging to the *Datisceœ*, and met with in the temperate and sub-tropical Western Himalayas from Kashmir to Nepal. The root, known as *Akalbir*, has been extensively used in Kashmir and throughout the Himalayas as a yellow dyestuff chiefly on alum-mordanted silk ; but the colouring matter appears to be present in the whole plant, for the leaves and twigs can also be employed for the same purpose.

The leaves of the *Datisca cannabina* were first examined by Braconnot (Ann. Chim. Phys. [2] iii. 277), who isolated from them a crystalline substance which he named datiscin. Somewhat later it was shown by Stenhouse (Annalen, 1856, 98, 167) that this compound is a glucoside, and when hydrolysed is converted into a sugar, together with a yellow colouring matter, *datiscetin* $C_{15}H_{10}O_5$.

Schunck and Marchlewski (Annalen, 278, 261), however, considered that ·the formula $C_{15}H_{12}O_6$ was preferable, and showed that, on fusion with alkali, datiscetin gives *salicylic acid*. By the action of dilute nitric acid, a *nitrosalicylic acid* was produced, whereas with strong nitric acid, picric acid, as already indicated by Stenhouse, was formed. Datiscetin appeared to contain methoxyl groups, and was at that time considered by the authors to be most probably a xanthone derivative.

Korczynski and Marchlewski (Ann. d. Akad. Krakau, 1906, 95) have shown that pure datiscetin $C_{15}H_{10}O_6$, however, does not contain methoxy-groups. It consists of yellow needles, m.p. 268°–269°, soluble in alkaline solutions, with a yellow colour, and gives, with sulphuric acid, a yellow liquid possessing a green fluorescence. When boiled with strong alkaline solutions, phenol and salicylic acid are produced.

Tetraacetyldatiscetin $C_{15}H_6O_6(C_2H_3O)_4$ forms colourless needles, and melts at 138° : and *tetrabenzoyldatiscetin* $C_{15}H_6O_6(C_7H_5O)_4$ gives colourless needles, m.p. 190°–191°.

Leskiewicz and Marchlewski (Ber. 1914. 47, 1599) by the action of bromine on datiscetin in boiling acetic acid solution obtained *tribromphloroglucinol*, and as a result suggest that this colouring matter is the 1 . 3 : 1'-trihydroxyflavonol :—
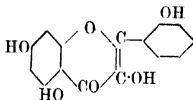
A substance indeed of this constitution in the form of its trimethyl ether has been synthesised by Bargellini and Peratoner (Gazetta, 1919, 49, 64) by the usual methods of flavonol synthesis. Thus 2 hydroxy 4 : 6-dimethoxy phenyl methyl ketone (phloracetophenone dimethyl ether) condensed with salicylic aldehyde methyl ether yields 2 hydroxy 4 : 6 : 2' trimethoxy phenyl styryl ketone I. :—

I. MeO⟨⟩—CO—CH : CH—⟨⟩
   MeO   OMe
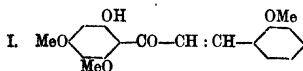
which by means of dilute alcoholic hydrochloric acid gives 5 : 7 : 2' trimethoxy flavanone II. :—

II. MeO⟨⟩ O CH—⟨⟩
    MeO   CO—CH₂   OMe
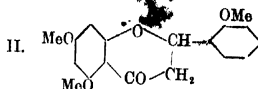
The iso-nitroso derivative of this latter when heated with hydrochloric acid in acetic acid solution gives the trimethoxy flavanone :—

MeO⟨⟩ O C——
MeO   CO—C·OH   MeO
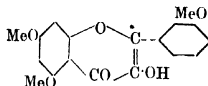
crystallising in pale yellow needles, m.p. 158°–160°, and giving with sulphuric acid an intensely green fluorescent solution. This is probably a trimethyl ether of datiscetin.

Datiscin $C_{21}H_{24}O_{11}$ (S. and M.), the glucoside crystallises in silky needles, which melt at about 190°, and dissolve in alkaline solutions with a yellow colour. Hydrolysis with dilute sulphuric acid yields datiscetin and *rhamnose*, not datiscetin and glucose, as stated by Stenhouse (*l.c.*).

The dyeing properties of datisca root on wool are very similar to those of old fustic. It is, however, slightly inferior in dyeing power. On cotton it dyes more like quercitron bark, in so far that the olives obtained on iron mordant are bluer in shade, as though some tannin matter were present. It appears to have about the same colouring power as quercitron bark, but gives a brighter yellow with aluminium mordant. Applied to wool, it differs from quercitron bark by giving with chromium mordant an olive-yellow which is not of such a reddish tinge, and with tin mordant a bright yellow instead of an orange. It is an excellent dyestuff, and worthy to rank with the natural yellow mordant colouring matters at present in use (Hummel and Perkin, J. Soc. Chem. Ind. 1895, 14, 458).

A. G. P.

DATISCIN v. DATISCA CANNABINA.

DATISCETIN v. DATISCA CANNABINA.

DATOLITE. A native boro-silicate of calcium $HCaBSiO_5$, containing B_2O_3 21·8 p.c. Monoclinic crystals, with a profusion of small brilliant faces, many with five-sided outlines, are of common occurrence ; these are usually transparent and colourless, or with a faint greenish tinge ; sp.gr. 3·0. The mineral most often occurs associated with zeolites in the amygdaloidal cavities of basaltic rocks, *e.g.* in the neighbourhood of Edinburgh and Glasgow, and at Bergen Hill and West Paterson in New Jersey. It, however, presents several other modes of occurrence, viz. in granite at Baveno in Piedmont ; in diorite at Rosskopf in Baden ; in gabbro with copper ores at Monte Catini in Tuscany ; in ' limurite ' (an axinite-pyroxenite) at Dundas in Tasmania ; in serpentine in the Lizard district in Cornwall ; in calcite veins in sandstone at Sonthofen in Bavaria ; in veins of silver ore at Andreasberg in the Harz Mountains ; in the Lake Superior copper mines (here in a compact, opaque, white form resembling unglazed porcelain) ; in beds of magnetite in gneiss at Arendal in Norway.

L. J. S.

DATURA STRAMONIUM v. TROPEINES.

DAUCINE C$_?$H$_{18}$N$_2$, colourless, oily base, b.p. 240°–250°, occurring in carrot leaves (Pictet and Court, ... 1907, 40, 3771), together with pyrrolidine.

DEAD DIPPING. The process of producing a pale-yellow dead surface on ornamental brass-work. The brasswork, after the final stamping, with its adhering black scale from the annealing oven, is placed in dilute nitric acid until the scale is detached, when it is removed and washed with water. It is next plunged into stronger nitric acid, and when its surface is covered with minute gas bubbles, it is washed in a solution of argol and dried in hot saw-dust.

DEAD OIL. The higher boiling fractions of shale oil, from which the greater portion of the solid paraffin has been crystallised out.

DECACYCLENE C$_{36}$H$_{18}$. A hydrocarbon obtained together with fluorocyclene C$_{48}$H$_{28}$ and chlorene C$_{48}$H$_{26}$ by heating acenaphthene with lead oxide at 370°–380° (Dziewonski and Suknarowski, Ber. 1918, 51, 457).

n-DECAHEXANEDICARBOXYLIC ACID CO$_2$H[CH$_2$]$_{16}$CO$_2$H. Prepared by the electro-lysis of an aqueous solution of the potassium salt of the monoethyl ester of suberic acid, and hydrolysing the diethyl ester thus formed (Brown and Walker, Annalen, 261, 125); m.p. 118°.

DECAMETHYLENEDICARBOXYLIC ACID CO$_2$H·[CH$_2$]$_{10}$·CO$_2$H. Prepared by heating the methyl ester of bromundecylic acid with alcohol and potassium cyanide, and hydrolysing the product with alcoholic potassium hydroxide (Nördlinger, Ber. 1890, 2357); m.p 124·5°–125·5°.

DECATOIC ACIDS C$_{10}$H$_{20}$O$_2$.

1. *Capric acid* CH$_3$(CH$_2$)$_8$COOH is found as a glyceride in the butter of the cow and goat, and in cocoa-nut oil, in association with caproic and caprylic acids. Many fusel oils also contain it (Fischer, Annalen, 118, 307; Grimm, *ibid* 157, 264; Rowney, *ibid.* 79, 236), and it is found as *iso*amyl caprate in certain Hungarian wines, and is formed by the oxidation or distillation of oleic acid (Redtenbacher, *ibid.* 59, 45), and by heating octylacetoacetic ester with alcoholic potash (Guthzeit, *ibid* 264, 5). A white crystal-line substance of m.p. 31·3°; b p. 268·4° (corr.); sp gr. 0·8858 at 40°/4°; possessing a goat-like smell; insoluble in cold water, but slightly soluble in boiling water.

2. *Di-iso-butylacetic acid*

$$[CH(CH_3)_2CH_2]_2CH·COOH$$

Obtained by heating di*iso*butylmalonic acid (Bentley and Perkin, Chem. Soc. Trans. 1898, 62); b.p. 225°–230° (730 mm.).

DECHENITE v. VANADIUM.

DECOIC ACID, CAPRIC ACID v. DECATOIC ACID.

DECOLOURISING CARBONS. This term has been applied to nearly pure forms of carbon, possessing remarkable decolourising powers, and manufactured only within the last ten years. In this article it will be convenient to group these special carbons separately from those which have been employed as decolorants for over a century.

(a) *Vegetable Charcoals.*

The decolourising property of wood charcoal was first observed by Löwitz in 1791, and was used for treating beet-syrup. An improved charcoal, produced by washing and grinding, was patented by Louis Constant in 1812, and employed in the refining of sugar. Wood char-coal is manufactured by burning wood in special ovens, or in heaps, air being excluded. Oven charcoal has the composition : carbon, 81 p.c. ; hydrogen, 4 p.c. ; oxygen and mineral matters, 15 p c. Charcoal burnt in heaps has the com-position : carbon, 90 p.c. ; hydrogen, 2·5 p.c. ; oxygen and mineral matters, 7·5 p.c. Klasen and Bergh (Chem. Zeit. 1910) state that the oven-charcoal absorbs 15 p.c. by weight of oxygen at 100° C. The decolourising power of most vegetable charcoals is very slight, but superior qualities are obtained from cherry stones, cocoanut, and certain grasses. But if wood be treated with certain chemicals before being carbonised, the resulting charcoal is a very efficient decolorant (*see* group (c) below).

(b) *Animal Charcoals.*

In 1811, Figuier proved that bone charcoal was a far more effective decolorant than wood charcoal. In 1815, Messrs. P. and J. Martineau patented the use of bone charcoal for refining and clarifying sugar solutions. In 1817, De Cavaillon patented the calcining of bone charcoal after it has been used as a decolorant, rendering it 'superior to new charcoal, and the operation may be repeated any number of times with equal effect' Up to the year 1828, bone charcoal was used in the form of fine powder, mixed with the liquid to be decolourised, and, finally, separated therefrom by filtration. Payen, in 1828, introduced an important im-provement, the 'bone-char' being produced in a granular form, permitting the syrup (or other liquid) to be filtered through the bone-char in 'char cisterns' or 'char filters,' first designed by Dumont. The granular charcoal acted as efficiently as the powder, and avoided the troublesome filtration to separate the powder from the liquid. The granular form was also more suitable for burning in order to restore its activity after it becomes charged with organic impurities absorbed from the liquid under treatment. Dumont's 'char filter' was of the open type, operating by gravity. The modern vessels are closed, and operate under pressure, and the same liquid may pass through two or even three filters, if necessary.

Formerly, bone-char was employed for decolourising both beet and cane juices, in order to produce white sugar direct from the plant. Less costly methods of purifying these juices have led to the abandonment of bone-char in the raw sugar factory, and its application in the refinery only.

Manufacture of Animal Charcoal. The bones employed should be carefully selected, hard, and free from extraneous matter. Whale and fish bones are not of a suitable character, as they yield a soft char. Bones which have been exposed to atmospheric action for a long time, or which have been buried in the ground, cannot be successfully employed, as, owing to the alteration in their composition, they produce a char deficient in carbon.

Before proceeding to carbonise the bones, the fat is removed by boiling, or by means of a suitable solvent such as benzene. By the first-named treatment from 4 to 5 p.c. of fat is extracted, and by the second from 8 to 12 p.c.

The crushed bones are carbonised in apparatus similar to that used in a gasworks, in vertical or horizontal iron retorts of a round, oval, or D section, the latter by preference. The length of the horizontal retort is usually from 8 to 10 feet, the long diameter being 18 inches and the short diameter of the oval retort 12 inches. There are usually five or seven retorts in each bed. The retorts are connected in the same way as gas retorts, with a hydraulic main, and this again with condensers or scrubbers filled with coke, in which the bone oil separates, and from which the gases are exhausted. The gases are then forced through a series of washers containing water to remove the ammonia, the residual gases, which are employed for heating and lighting purposes, finally passing into a gas-holder. Charges of about 2½ cwt of bones are carbonised in vertical, and 5 cwt. in horizontal retorts, the operation taking about 6 to 8 hours with the former, and 8 to 10 hours with the latter. The bone oil, collected in the condenser, amounts to from 3 to 5 p.c. on the bones carbonised, and the ammonia in the ammoniacal liquor is equal to about 8 p.c. of ammonium sulphate, into which it is converted in the usual way. When the bones are completely carbonised, the charcoal is removed from the retorts and cooled in strong sheet-iron canisters, which are at once covered with closely fitting lids and luted round the edges, either with charcoal paste, or a water lute. The char, when quite cold, is crushed in a suitable mill (any iron it may contain being removed by passing over the poles of an electro-magnet), and then sifted into various sizes to suit the requirements of the sugar-refiner. It is usually moistened before grinding, to keep down the dust. Good bones yield about 65 p.c. of char, but from 20 to 30 p.c. of this is dust, which fetches a lower price than the larger grist.

The following is the approximate composition of a good sample of new bone charcoal :—

Carbon . . • . . .	10·51
Calcium and magnesium phosphates, calcium fluoride, &c.	81·21
Calcium carbonate . . .	7·30
Calcium sulphate . . .	0·17
Ferric oxide . . .	0·12
Silica	0·34
Alkaline salts . . .	0·35
	100·00

Moisture originally present . 8·00

Space occupied by one ton, 48 cubic feet.
Weight of char left on sieves of various degrees of fineness :—

Above 10 holes to linear inch	.	0
10 to 20	,,	,,	,,	. 28
20 to 30	,,	,,	,	. 32
30 to 40	,,	,,	,,	. 27
40 to 50	,,	,,	,,	. 11
Through 50	,,	,,	or dust	2
				100

New charcoal of good quality should, in the dry state, contain not less than 9 and not more than 11·5 p.c. of carbon. The silica should not exceed 0·5 p.c., the oxide of iron 0·15 p.c., the calcium sulphate 0·2 p.c., and the moisture 8 p.c. Its weight should not exceed 52 lbs. per cubic foot. It should be of a dull black colour, and, when incinerated, leave an ash of a uniform white or cream colour ; the presence of grey or reddish particles indicates that the sample has been mixed with old charcoal. When brought in contact with the tongue, it should adhere to it somewhat strongly. The size of grain depends upon the use to which it is to be applied. Large-grain charcoal is preferable for strong liquors, such as that used for washing loaf sugar. Refiners, as a rule, prefer small grain ; if, however, it be very small, it impedes the passage of liquor and also gives considerable trouble in washing. Char may be used over and over again, and sometimes lasts several years, being revivified from time to time by reburning in special kilns (see SUGAR). When, by continued use, it has lost its power of removing colour, it is known as spent char, and is then used as a manure, generally after treatment with sulphuric acid, so as to form superphosphate of lime.

The carbon always contains a certain proportion of nitrogen, amounting to about one-tenth of its weight ; also a minute proportion of hydrogen The nitrogen present decreases whilst the bone charcoal is being used for sugar-refining.

When char is repeatedly reburned, it becomes less porous and shrinks in volume, so that a ton, which measures 48 to 54 cubic feet when new, may be reduced to 28 cubic feet after being reburned many times ; in other words, its apparent density may be nearly doubled.

Wallace has, however, shown that the real sp.gr. varies but little ; thus, a new char, occupying 50·6 cubic feet per ton, or having an apparent sp.gr. of 0·71, has a real sp.gr. of 2·822, whilst a moderately old sample, occupying 35 cubic feet per ton, or having an apparent sp.gr. of 1·03, has a real sp.gr. of 2·857, or only a trifle over that of the new.

Another proof that char loses its porosity by long-continued use and reburning, is afforded by the fact, pointed out by Wallace, that dry new char will absorb from 80 to 100 p.c. of its weight of water, whereas old char will only retain from 30 to 45 p.c.

Properties.—Although the decolourising property is the most important, bone-char absorbs other organic and mineral substances from their solutions. Tilbot was the first to prove that the absorption of organic matter increases with the temperature, and Kohlrausch first demonstrated that the absorbed colouring matters remain chemically unchanged, and can be extracted from the charcoal by washing it with ammonia, in which the colouring matters dissolve. It was proved by Graham that various mineral substances are removed from solution by animal charcoal ; thus the lime is taken up from lime water, and metallic salts are absorbed from their solutions in water. According to Chevallier, lead nitrate and acetate are completely removed by animal charcoal. Weppen has shown that this action extends to a great variety of metallic salts, including cupric, zinc,

chromic and ferrous sulphates, nickel, cobalt, silver, mercurous and mercuric nitrates, tartar emetic, stannous chloride, and ferric acetate.

As the result of a number of experiments on the absorption of different salts by animal charcoal, Bodenbender arrived at the following conclusions :—

1. The power of absorbing salts is a physical property.

2. A given weight absorbs a larger proportion of salts from a concentrated than from a diluted solution ; on the other hand, the proportion absorbed from a constant quantity of salts is more considerable when this quantity is in a dilute, than when it is in a concentrated, solution.

3. The presence of sugar has only a slight influence on the absorption of salts.

4. The salts of potassium are absorbed in smaller proportion than those of sodium.

5. Among the salts experimented with, the amount taken up is in the following order, beginning with that least absorbed : potassium chloride, sodium chloride, potassium nitrate, sodium nitrate, potassium acetate, sodium acetate, potassium sulphate, sodium sulphate, magnesium sulphate, potassium carbonate, sodium carbonate, sodium phosphate.

6. A chemical action of charcoal has been observed with respect to some carbonates, oxalates, and other salts, being brought about by the presence of calcium sulphate and phosphate in the charcoal.

7. Charcoal, saturated with one salt, is capable, within certain limits, of withdrawing another salt from solution.

8. There is less absorption of a salt when the contact is brief than when the contact is prolonged. The difference due to time of contact ceases when the contact has lasted some hours.

Investigations by W. B. Clark (J. Soc. Chem. Ind. 1912, 262) indicate that the decolourising power of bone-char depends very largely on the quantity of mineral matter and reducing sugar in the liquor treated in the sugar refinery. The first portion of syrup leaving the char filter contains only about 60 p.c. of the reducing sugar, and 30 p.c. of the mineral matters originally in solution. After these have been absorbed by the char, they are subsequently set free, so that the final portions of syrup contain even more reducing sugar and mineral matters than were originally in solution. At this stage there is a gradual decrease in the decolourising power of the char. After the syrup inlet has been closed, hot water is passed through the char to displace the syrup. In this wash-water, the reducing sugars and mineral matters are present in considerable quantities. This washing treatment restores the normal activity of the char, although the washed char still contains much organic matter, which can be extracted by means of caustic soda solution. Clark remarks that the behaviour of char closely resembles diffusion, the char itself acting as a dialyser, permitting the crystallisable sugar to diffuse through it more rapidly than the other substances present. Bone-char attains its maximum efficiency after being used, washed, and burnt several times. The porosity is thereby reduced, as also is the percentage of organic matter other than carbon, and the percentage of calcium carbonate is reduced from about 9 to 3 p.c. The residual calcium

exists as a basic phosphate, which is partially decomposed by heating the char with dilute acids, causing an increase in decolourising power.

New char exerts a slight oxidising action on colouring matters which are not absorbed by it. Degener and Lack state that freshly ignited bone-char, moistened with water, and exposed to light and air, produces a perceptible quantity of hydrogen peroxide, and is thus rendered more active than the untreated char. If milk of lime be sprinkled over the char, calcium peroxide is produced. ·

The high decolourising power of bone-char relative to wood charcoal was formerly supposed to be due to the presence of 5–7 p.c. of nitrogen in the former, and only traces in the latter ; but this view has now been abandoned in favour of a physical, or purely mechanical, action.

Charcoal prepared from flesh has about the same decolourising efficiency as that made from bone. Blood charcoal is less efficient. Fish charcoal is the subject of a patent by Adler, 1913. The finely minced fish is boiled with water, carbonised, and the resulting charcoal washed with hydrochloric acid.

(c) *' Decolourising Carbons.'*

As stated under (a), very active carbons can be obtained from various woods when these are chemically treated before being carbonised. The earliest patent appears to be that of R. von Ostrejko, in August, 1900, for treating wood powder with calcium chloride or magnesium chloride before carbonising, and subsequently treating the carbon with acid to extract the lime. In a later patent, October, 1900, he employs calcium acetate or chloride, and starch mucilage. Subsequent patentees employ sulphuric acid at 200° C. (Halse, 1902) ; earthy lignites treated with kaolin (Goldstein, 1907) ; carbonaceous matter of animal or vegetable origin is ignited in the presence of chlorine gas (Molenda and Wunsch, 1912) ; peat treated with hydroxides or carbonates of potassium, sodium, calcium, or barium (Kruszewski, 1912) ; wood treated with zinc chloride (Wunsch, 1913) ; wood treated with calcium oxide or carbonate (Bonnard, 1914).'

Two very successful carbons are the Dutch ' Norit ' and the German ' Eponit.'

' *Norit* ' is a fine black powder, containing 94–96 p.c. carbon, and 4–6 p.c. mineral matter. It possesses about 30 times the decolourising power of bone-char, and about 100 times that of wood charcoal. The activity increases in the presence of acids, but diminishes in the presence of alkalis.

' *Eponit* ' is also a fine powder, containing carbon, 86·5 p.c. ; mineral matters, 4·1 p.c. ; and moisture, 9·4 p.c. Experiments by Ströhmer indicate that it possesses 10 times the decolourising power of bone-char, and is not influenced by the acidity or alkalinity of the liquid treated. From his chemical and microscopical examination he concludes that ' Eponit ' is a carbonised vegetable substance, probably wood.

More recently, a Committee of the Royal Society of London has investigated this carbon, and attempted to reproduce it by carbonising various kinds of wood. The conclusion arrived at was that ' Eponit ' is made from a mixture

of coniferous wood, such as pine or cedar, and angiospermous wood, such as poplar or willow.

Following Ostrejko's patent (*see* above), the Committee carried out the following experiments :—

(*a*) A mixture of pine and willow woods was treated with calcium acetate and starch, carbonised at a white heat, and the resulting carbon boiled with hydrochloric acid, washed with water, and heated to a red heat in a retort.

(*b*) Cedar wood was treated with calcium acetate alone, before carbonising, and the same subsequent treatment.

Both (*a*) and (*b*) proved superior to ' Eponit.' Further experiments with cedar and willow were conducted as follows : (*a*) untreated ; (*b*) treated with milk of lime ; and (*c*) with calcium acetate before carbonising at a white heat, subsequent treatment as before. The following results were obtained : (*a*) both charcoals were useless for decolourising purposes ; (*b*) and (*c*) both woods gave very active charcoals, equal to ' Eponit,' (*c*) being slightly superior to (*b*). The Committee concluded that the type of wood has little or no influence on the result, and that probably any porous wood, after similar chemical treatment, would yield an active charcoal. Further, that the treatment with milk of lime is less costly than that with calcium acetate, and the resulting carbon is practically equal in decolourising power.

Pellet (Bull. Assoc. Chim. Sucr. 1916, **33**, 220–227) has studied the relative decolourising powers of numerous carbons and charcoals relative to ' Eponit ' taken as standard. He employed a dilute solution of molasses, previously clarified with basic lead acetate and the clear solution acidified with (*a*) hydrochloric ; and (*b*) sulphurous acids. As some of the carbons gave slightly different values in the presence of these different acids, the two following series were obtained, in which ' Eponit ' is the most efficient :—

(*a*) With hydrochloric acid : Eponit, 1 ; Littoral, 2 ; Flandrac, 3 ; Flaming, 4 ; special carbon for wines, 5 ; bone-char, 6 ; special carbon, 7 ; bone-char washed with acid, 8 ; cherry stone carbon, 9.

(*b*) With sulphurous acid : Eponit, 1; Flandrac, 1 ; Littoral, 2 ; special carbon, 3 ; special carbon for wines, 5 ; bone-char washed with acid, 6 ; Flaming, 7 ; bone-char, 8 ; cherry-stone carbon, 9.

' Norit ' and ' Eponit ' resemble bone-char in absorbing organic and mineral matters from the solutions treated by them, and thus gradually losing their activity. This can be restored by two methods : (*a*) carbonising, so as to destroy the organic matter ; and (*b*) by boiling with dilute caustic soda, which dissolves the organic matters, after which the carbon is separated in a filter-press, and washed with hot water until free from alkali.

In the former method, a special type of kiln must be employed (Wijnberg's Patent, 1916). The second method was patented by Wijnberg and Sauer in 1911 and 1912, and requires no special plant, but appears to have been applied to bone-char many years previously. In another patent by Wijnberg, in 1915 Norit is employed to facilitate filtration of sugar juices through cloth-filters, owing to its power of absorbing gums and pectins.

(*d*) *Mineral Carbons.*

Coal, or other bituminous substance, is impregnated with an alkali, or alkali carbonate, and some time later with an acid ; or first with acid, and later with alkali, before ignition in retorts (Lotz, D. R. P. 1911). ' Culm,' a bituminous mineral present in the alum slate of Sweden, is dry distilled, the residue leached with acid, and washed with water. It can be regenerated by washing and re-heating (Hellsing, Eng. Pat. 1913). Coal is heated with excess of anhydrous zinc chloride in an open vessel until the chloride begins to volatilise. The mass is cooled, crushed, washed in a filter press with dilute hydrochloric acid, and finally with water (Wunsch, Eng. Pat. 1914). The residue from shale-oil distillation is carbonised (Catlin, U.S. Pat. 1917).

(*e*) *Carbons produced from Industrial By Products.*

Clacher claims that an active carbon can be prepared from ' bagasse, 'or crushed sugar cane, after the extraction of the juice (Int. Sugar Journ. 1914, **64** 66). The Pan Chemical Co., U.S.A , manufacture an active carbon from the by-product obtained in the manufacture of salts of tartaric acid from argol. This residue contains 50 p.c. moisture, and 50 p.c. crude fibre with lime and sand. It is dried and heated in retorts (U.S. Pat. 1912). Mathéus (Papierfabrikant, 1911, 9, 1435) evaporates sulphite waste lyes with milk of lime to a thick syrup, and finally in flat vessels, until it solidifies, forming a brittle mass. This is powdered and heated in a closed vessel.

' Black ash residue,' obtained by evaporating the alkali separated from wood pulp, consists mainly of carbon with 1-5 p.c. of ash. The percentage of ash can be reduced to about 0·8 p.c. by washing the residue with hydrochloric acid. The washed carbon has ten times the decolourising power of bone-char (McKee, U.S. Pat. 1914). T. H. P. H.

DÉGRAS, or **SOD OIL,** is the waste fat obtained in the chamoising process, and is used for currying purposes, *i.e.* dressing bark-tanned or chrome-tanned leather. The skins which are to be converted into chamois leather, are first ' limed,' the hair is then removed and the unhaired hides are ' drenched,' *i.e.* placed in a ' sour bath,' in which the free lime is neutralised through the development of an acid fermentation, caused by *Bacillus furfuris.* The skins are then stretched and well rubbed with whale oil, or cod (liver) oil, in the United States with menhaden oil, and worked in ' stocks,' so as to become thoroughly saturated with the oil. The skins are then exposed to the air, and the process of rubbing with oil and stamping in the stocks is repeated until enough oil has been absorbed. By exposure to the atmosphere, a portion of the oil becomes changed, and is most likely converted into the glycerides of ' oxidised ' acids. In order to promote the oxidation of the oil, the skins are heaped together in a warm room, and covered carefully with canvas, so as to keep the generated heat in the heap whereby a large proportion of the oil is converted into ' oxidised ' oil. The bulk of the oil is expressed from the skins by pressure, the remainder of the

oil retained by the skins being removed by one of the two following methods, known respectively as the English and German method, or the French method. In the English and German method, the skins are washed with alkaline lyes; the emulsion thus obtained is acidified with sulphuric acid, when the fatty matter separates and is skimmed off. This fatty substance forms, the 'sod oil' of commerce. In the French method, the skins are 'stocked,' aired, and 'fermented' for a shorter period than in the English or German method, so that a large proportion of the oil can be obtained from the skins by steeping them in warm water, and wringing or pressing in hydraulic presses. The oil thus obtained is termed 'première torse moëllon.' The oil still retained by the skins is recovered by washing with alkaline lyes, as is done in the English and German method, and the fatty matter so recovered is usually added to the moellon An addition of other oils is also made to moellon, and for this reason the commercial product contains less fibre and mineral matter than sod oil.

The most characteristic constituents of dégras are the oxidised fatty acids.

According to Jean, the characteristic oxidation product is a resin-like body melting at 65°–67°. This substance is insoluble in petroleum spirit, but dissolves in alkaline solutions, from which it is again precipitated on the addition of acid. It has been termed *dégras former* by Simand, and has been shown by Fahrion to be composed of a mixture of hydroxy acids and anhydrides.

Dégras is largely admixed with fish oils, blubber oils, tallow of low quality, &c. According to trade custom, such products are considered as a genuine product. On the other hand, the numerous substitutes of dégras, or *artificial dégras,* which occur in commerce, consist of highly adulterated dégras, the adulterants being mineral oils, wool fat, or blown blubber oil, and rosin. Analyses of dégras and sod oils of different kinds are given in J. Soc. Chem. Ind. 1891, 10, 557; 1892, 11, 639; and J. Amer. Chem. Soc. 1899, 21, 291.

<div align="right">J. L.</div>

DEHYDROTHIO-*p*-TOLUIDINE, DEHYDRO-THIO-*p*-TOLUIDINE SULPHONIC ACID, *v.* PRIMULINE AND ITS DERIVATIVES.

DEHYDROTHIO-*m*-XYLIDINE
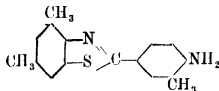
is prepared by heating *m*-xylidino with sulphur until hydrogen sulphide ceases to be evolved (*cf.* Dehydrothio-*p*-toluidine; Art. PRIMULINE). The excess of *m*-xylidine is removed by distillation and the residue treated with hydrochloric acid, in which the *iso*dehydrothio-*m*-xylidine (m.p. 121°), formed simultaneously, is insoluble; m.p. 107°; b.p. 283°/14 mm. Insoluble in water, readily soluble in hot alcohol (Anschütz and Schultz, Ber. 1889, 22, 582; Paul, Zeitsch. angew. Chem. 1896, 9, 679).

DELPHINE BLUE, *v.* OXAZINE COLOURING MATTERS.

DELPHINIDIN, DELPHININ, *v.* ANTHO-CYANINS.

DELPHININE $C_{31}H_{49}O_7N$ is one of a series of ill-defined poisonous alkaloids, including *delphisine, delphinoidine, staphisagroine,* and *staphisagroidine,* found in stavesacre seeds (*Delphinium Staphisagria* (Linn.). Official in the B. P. and U.S. P. (Kora-Stojanoff, Chem. Zentr. 1890, [ii.] 628, and Ahrens, Ber. 1899, 32, 1581, 1669.) *Delphinium consolida* and *D. ajacis,* according to Keller (Arch. Pharm. 1910, 248, 468; 1913, 251, 207), also contain alkaloids. From various *Delphinium* spp Heyl has obtained 'delphocurarine,' an amorphous mixture of bases, including a crystalline substance, m.p. 184°–185° (Chem. Soc. Abstr. 1903, i. 650) 'Delphocurarine' resembles curarine in physiological action (Lohmann, Pflug. Arch. 1902, 92, 398).

DELPHINIUM CONSOLIDA. *Delphinium consolida* is a common European plant belonging to the Larkspur family; its name refers to its powers, real or imaginary, of healing or consolidating wounds. The blue flowers were examined by Perkin and Wilkinson (Chem. Soc. Trans. 1902, 81, 585) to determine if these yield the same colouring matters as those previously isolated from the flowers of the *D. zalil* (*ibid.* 1898, 73, 267). The presence of kaempferol only could, however, be detected. For its isolation an aqueous extract of the flowers was digested at the boiling-point with addition of sulphuric acid, and the brown resinous product which separated on keeping, extracted with alcohol and the extract evaporated to a small bulk. Addition of ether to this solution caused the precipitation of resinous impurity, and on evaporating the ethereal liquid a semicrystalline residue of the crude colouring matter was obtained. The product was crystallised from dilute alcohol, converted into acetyl derivative, and this after purification retransformed into colouring matter in the usual manner The yield was approximately 1 p.c.

Kaempferol $C_{15}H_{10}O_6$ consists of yellow needles, m.p 276°–277°, soluble in alkaline solutions with a yellow colour. These liquids on exposure to air are slowly oxidised with development of a brown tint.

Tetra-acetylkaempferol $C_{15}H_6O_6(C_2H_3O)_4$, when crystallised from methyl alcohol forms colourless needles, and when heated commences to melt at 116° and becomes completely fluid at 120°. On further heating, however, gradual solidification ensues and the product subsequently melts at 181°–182°. This peculiarity of acetylkaempferol, which is not apparent when the substance is crystallised from ordinary alcohol, affords a convenient method for its detection.

Tribromkaempferol $C_{15}H_7Br_3O_6$ forms yellow needles, m.p. 275°–277°; *kaempferol sulphate* $C_{15}H_{10}O_6$SO_4, orange-red needles; *kaempferol hydriodide* $C_{15}H_{10}O_6$HI, needles, and *monopotassium kaempferol* $C_{15}H_9O_6K$, orange-yellow prismatic needles.

Kaempferide, a monomethyl ether of kaempferol, exists in Galanga root, and a monomethyl ether, apparently distinct from this latter, has been isolated from the berries of the *Rhamnus catharticus.* The glucosides at present known of kaempferol are *robinin,* which occurs

in the flowers of the *Robinia pseudacacia*; *kaemp-feritrin*, found in the leaves of the *Indigofera arrecta*; and *kaempferin*, which has been isolated from senna.

Fused with alkali, kaempferol gives *phloro-glucinol* and p-*hydroxybenzoic acid*.

To kaempferol v. Kostanecki assigned the constitution of a *trihydroxyflavonol* (Ber. 1901, 34, 3723) :—
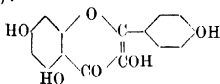
and its synthesis was subsequently effected by v. Kostanecki and Tambor (Ber. 1904, 37, 792).

2-*Hydroxy*-4 : 6 : 4'-*trimethoxychalkone* (1) when digested with boiling dilute alcoholic sulphuric acid gives 1 : 3 : 4'-trimethoxy flavanone (2) :—
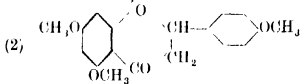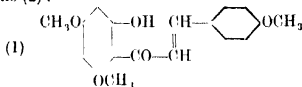
and the latter by means of amyl nitrite and hydrochloric acid is converted into *iso-nitroso*-1 : 3 : 4'-*trimethoxyflavanone* (3).

When a solution of this substance in acetic acid is boiled with 10 p c sulphuric acid 1 : 3 : 4'-*trimethoxyflavonol* (4) is produced, from which by the action of hydriodic acid *kaempferol* (5) is readily prepared :—
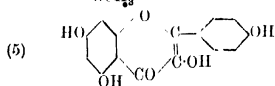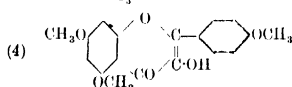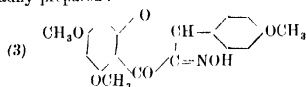
Kaempferol possesses well-defined dyeing properties, and gives with mordanted woollen cloth the following shades which closely resemble those given by morin :—

Chromium.	Aluminium.
Brownish-yellow.	Yellow.
Tin.	Iron.
Lemon-yellow.	Deep olive-brown.

It is also present in the *Impatiens balsamina* (Chantili Pass), the *Erythrina stricta* (vernacular name 'Kon kathet') (Perkin and Shulman, Chem. Soc. Proc. 1914, 30, 177), the berries of the *Rhamnus catharticus* and together with quercetin, both apparently as glucosides, in the flowers of the *Prunus spinosa* (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 56). For the separation of the two colouring matters a fractional crystallisation from acetic acid was

employed, kaempferol in these circumstances being the more sparingly soluble. A. G. P.

DELPHLEGMATOR. An apparatus used in fractional distillation. The term is also employed in distilleries for an apparatus for freeing alcohol from water (*phlegma*).

DELTA ACID. Disulpho acid S. 1-Naph-thylamine-4 : 8-disulphonic acid.

DELTAPURPURIN *v.* Azo- COLOURING MATTERS.

DENATURANTS. This term is applied to substances which are added to articles usually subject to revenue imposts, and primarily intended for human consumption (as spirits, tobacco, &c.) in order to render such articles unfit for human consumption, but without impairing their efficacy as raw material for use in various arts and manufactures. Articles thus 'denatured' may safely (from a revenue point of view) be released from revenue control without payment of duty.

The principles underlying the choice of suitable denaturants are mainly as follows :—

(*a*) They should be inexpensive, so as not to add materially to the cost of the denatured article;

(*b*) Their use should cause the minimum amount of inconvenience to the manufacturer, both in regard to his processes and the necessary revenue supervision involved ;

(*c*) The denaturant should not be incompatible with the process of manufacture or the subsequent use of the denatured article ;

(*d*) It should be of such a nauseous and repugnant character as to remove any temptation to would-be consumers of the denatured article ; and

(*e*) The denaturant should have such a relation to the original article both in quantity and character as to preclude its removal from the mixture by any process which could be profitably carried out on a commercial scale, and it should be capable of being readily detected even if present in very small quantity.

In the United Kingdom the dutiable articles allowed to be denatured are *tea*, *tobacco*, *wine*, and *spirit*, the last being by far the most important, both by reason of the large amount of revenue derived from it, and the great variety and extent of its applications in the arts and manufactures.

Tea, before being admitted for consumption in the United Kingdom, is examined by the Customs under sect. 30 of the Sale of Food and Drugs Act, 1875, and, if found satisfactory, is passed on payment of duty : but if otherwise, it is refused admission as 'tea.' Since, however, it still possesses a certain commercial value as a raw product for the extraction of theine or caffeine, the Commissioners of Customs and Excise usually permit it to be admitted for this purpose duty free, after it has been effectively denatured in such a way as to make it unsuitable for use as a beverage, but without interfering with its efficacy as a source of caffeine. The same applies to those teas which have been accidentally damaged and are voluntarily withdrawn by the importers from sale as ' tea.'

In the case of tea, the denaturing process consists in grinding and mixing the tea with lime and asafœtida in the proportions of 1 part of asa-fœtida and 100 parts of lime to 1000 parts of tea.

Tobacco is dutied on the whole leaf, of which certain portions, as the midribs or so-called 'stalks,' are by manufacturers treated as waste or 'offal,' and the same applies to the unused portions of manufactured tobacco, known as 'shorts' or 'smalls.' On these the duty which has been paid is returned as 'drawback' to the manufacturer on condition, either that the tobacco offal is surrendered to the Government for destruction, or (if intended for such purposes as the manufacture of nicotine, insecticides, sheep dips, &c.), that it is denatured according to certain prescribed formulæ, and under the supervision of revenue officers. Denaturing is equally necessary in the case of offal from tobacco manufactured in bond (although no duty has been paid nor drawback given), in order to prevent its fraudulent use as a substitute for duty-paid tobacco.

The following formulæ have been officially approved in the United Kingdom for denaturing certain preparations having tobacco as a basis :—

" (*a*) *Sheep wash.* To every 100 lbs. of tobacco are added 10 lbs. of blue vitriol, 15 lbs. of common salt, 2 lbs. of oil of turpentine.

(*b*) *Tobacco extract* manufactured in bond may be denatured by adding 30 parts of soft soap to 70 parts of extract.

(*c*) *Hop powder.* To every 75 lbs. of snuff or tobacco are added 28 lbs. of sulphur, 5 lbs. of asafœtida, and 3 lbs. of sago flour.

(*d*) *Fumigant* for horticultural purposes. To every 100 lbs. of tobacco or snuff are added 10 lbs. of ground hellebore, 18 lbs. of saltpetre, 6 lbs. of asafœtida, 4 lbs. of cayenne, 2 lbs. of lampblack, 10 lbs. of sago flour.

Wine which has become unsound and sour (owing to the formation of acetic acid) so as to be no longer suitable for use as a beverage, is released from revenue custody after being denatured with a view to its conversion into wine vinegar. The denaturant used in this case is 20 p.c of commercial vinegar, or an equivalent quantity of acetic acid.

(For methods of denaturing alcohol, *v.* *Methylated spirits* and *Industrial alcohol,* art. ALCOHOL.) J C.

DENITRIFICATION *v.* FERMENTATION AND SOILS.

DENSIMETER *v.* SPECIFIC GRAVITY.

DENTALONE. A solution of chloretone in essential oils.

DERMATOL. Bismuth subgallate (*v.* BISMUTH, ORGANIC COMPOUNDS OF ; *also* SYNTHETIC DRUGS).

DERMOGEN. A trade name for zinc peroxide.

DERMOL. Bismuth chrysophanate. A yellowish - brown powder, said to have the composition $Bi(C_{15}H_9O_4)_3Bi_2O_3$. According to Merck, it is a mixture of impure chrysarobin and bismuth hydroxide (*v.* BISMUTH ORGANIC COMPOUNDS OF ; CHRYSAROBIN and SYNTHETIC DRUGS).

DERRIS ULIGINOSA (Benth.). The stem of this species of derris, used in the Far East as a fish poison, contains a poisonous resin (Proc. Amer. Pharm. Assoc. 1902, 50, 296).

DESAEGIN ('Colloidal chloroform'). An albuminous substance containing chloroform.

DESCLOIZITE. A basic lead and zinc vanadate, $(Pb,Zn)_2(OH)VO_4$, crystallising in the orthorhombic system, and isomorphous with olivenite (basic copper arsenate). A small amount of copper is sometimes present. The small crystals are deep reddish-brown in colour, and the streak is a paler yellowish-brown. It occurs in veins of lead ore in association with vanadinite, &c., and has been mined to a limited extent in New Mexico and Arizona, as a source of vanadium. It also occurs in considerable quantities in the Sierra de Cordoba in Argentina, and at Broken Hill in North-Western Rhodesia. L. J. S.

DESICCATION AND DRYING. The removal of mechanically admixed water from substances. The removal of chemically combined water is usually termed *dehydration,* but it is not always possible to draw a sharp distinction between the two processes.

A substance may be termed 'dry,' even though it still contains mechanically admixed water, provided that this water is not apparent to the touch ; the term 'desiccation' refers, strictly speaking, to the complete removal of admixed water.

The importance of drying and desiccating will be appreciated by a consideration of the numerous reasons for which these processes have to be employed, among which the following may be mentioned :—

1. To preserve material from undergoing physical and chemical alterations, *e.g.* leather, tobacco, fruit.

2. To remove water needed in preceding operations, *e.g.* drying coal after washing, woollen and cotton goods after dyeing, &c.

3. To facilitate accurate sampling, since substances are much more readily and uniformly mixed in the dry state than in the moist condition.

4. To diminish the weight of an unnecessary ingredient and thereby diminish cost of packing, carriage, and freight ; *e.g.* timber, peat, &c.

5. To retain desirable moisture in a substance by drying its surface, thereby rendering the outer layer impervious to moisture, *e.g.* the drying of soaps and chocolates:

6. To prevent injury to health or goods, as in the case of the moisture-laden air of textile factories, evaporating rooms, &c.

7. To prevent waste of heat in vapourising water when combustibles are burnt.

A slight consideration of the various purposes served by drying processes is sufficient to bring out the wide range of degrees of dryness, and the various conditions to which the term 'dry' is applied. This vagueness arises partly from the difficulty of stating quantitatively the amount of water present in a given instance, and partly owing to the varying capacity that substances possess for absorbing moisture. Thus it is that in ordinary conversation substances are variously described as 'soaked,' 'wet,' 'moist,' 'damp,' 'dry,' 'dried,' 'desiccated' or 'dehydrated,' in order to indicate qualitatively their degrees of dryness.

The drying processes in use may be classified under the following headings, corresponding with the degrees of drying to which they lead :—

A. Gravitational drying, by draining, filtering, absorbing, and condensing.

B. Mechanical drying, by pressure and centrifugal force.

C. Drying by evaporation.

A. Gravitational drying. The processes included under this heading are usually only preliminary to the employment of method C above.

Drainage is a natural process occasionally used for the purpose of removing surface water, e.g. from washed coal. The procedure requires no special description.

Decantation is a process by which solid substances mixed with a large amount of water are separated from the greater portion of that liquid by allowing them to settle, and running off the liquid from above the sediment. In practice it is often the custom to arrange 'settling tanks' in series, stepwise, and gradually feed the mixture of liquid *plus* suspended solid into the upper vessel by means of a pipe leading to the bottom. The overflow runs into the second vessel, and so on throughout the series. Arrangements are provided for emptying each tank as required. China clay, chalk, and barytes are separated in this manner.

Filtration is a process of accelerated drainage. Thus wet pigments prepared by precipitation are drained on calico sheets stretched loosely over a skeleton framework. Filtration is greatly accelerated by partially exhausting the air from the chamber into which the liquid drains. A vacuum filter has been designed to work continuously, and consists of a hollow drum, mounted with its axis horizontal, and partly submerged in a tank containing the suspension to be filtered. The periphery is covered with filter cloth, and the water is drawn by suction, applied to the interior of the drum, through this cloth, leaving the solid matter as an outside coating. By slowly revolving the drum, a continuous coating of solid is thus formed, and, after it reaches a certain thickness, an adjustable skimmer removes the surplus. This arrangement can be adapted to many drying operations, and consumes very little power.

Absorption is a drying process in which the material is dried by causing it to yield its moisture to other substances which are capable of annexing it. This process is not often applied on a large scale, although it is commonly employed in the laboratory. Instances are furnished, however, in the preliminary drying of large clay ware in dried plaster of Paris moulds, and in the drying of the highly water-laden atmospheres of evaporating rooms, dye houses, &c., by pumping warm, fresh air into them. Warm air having a much higher capacity for holding water vapour than cold air, the result is naturally to effect a drying of the atmosphere, besides warming up the room and fittings.

In the laboratory, substances are frequently dried by placing them in a *desiccator*. This is simply a closed glass vessel containing in a suitable receptacle some chemical compound, such as anhydrous calcium chloride, concentrated sulphuric acid, or phosphoric anhydride, which has a remarkable affinity for water, so that it will, by absorption, remove water vapour from the interior even when the tension of the aqueous vapour therein is exceedingly small. The substance to be dried being placed in the desiccator, in the interior of which the tension of aqueous vapour is almost *nil*, it gives off its moisture, and this is continuously absorbed by the desiccating agent employed. The latter must expose a large surface for rapid absorption

to occur. The velocity of drying in a desiccator may be greatly increased by exhausting the air from the interior (vacuum desiccator), since the rate at which moisture can diffuse from the material to the absorbing agent is thereby largely augmented. The degree of drying attained cannot, however, be increased, since that is limited merely by the pressure of the aqueous vapour when it has reached equilibrium with the absorbing agent. The rapidity of drying is also increased by placing the material to be dried at the bottom and suitably arranging the desiccating material above it. This arises from the fact that moist air has a smaller density than dry air at the same temperature and pressure; consequently, the natural process inside the desiccator is for the moist air to rise. The error in design exhibited in most laboratory desiccators, in which the above arrangement is reversed, was pointed out by Hempel (Ber. 1890, 23, 3566), to whom the desiccator shown in Fig. 1 is due. In this desiccator, the drying agent is placed in the trough of the lid.

It is usual to evacuate laboratory desiccators by means of the water-pump, but it may be easily accomplished by simple chemical means (J. Amer. Chem. Soc.

FIG. 1.

1906, 28, 834 ; Amer. Chem. J. 1902, 27, 340).

A desiccator for drying by means of a current of air has been described by Pratt (J. Amer. Chem. Soc. 1917, 39, 271). It consists of a Buchner funnel connected below, through
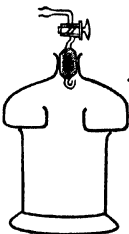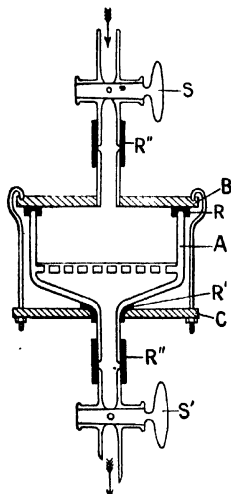
FIG. 2.

cock S', to a safety flask, which in turn is connected with a pump. Resting on the funnel is

a heavy brass disc, B, on the lower surface of which is cemented a ring or sheet of rubber, R, to make a tight joint. Pressure is brought to bear on the disc by means of three screws acting between the disc and a metal collar, C. Heavy rubber tubing, R', prevents the collar from exerting unequal pressure on the funnel. In the centre of the disc is set a brass tube, to which is attached, by means of heavy rubber tubing, R'', the cock S'. This cock is further attached to a system of drying-bottles or towers. The material to be desiccated is either filtered into or placed in the funnel (Analyst, 1917, 156).

Condensation.—This is employed as a means of drying materials which must be handled at low temperatures, and is a method adopted in cold storages. The principle of the process is, briefly, that the moist air of the rooms is drawn out and passed into chambers maintained at a very low temperature, where it is made to deposit the greater part of its moisture as a liquid. The dry air is then returned to the drying rooms, either cold, when it warms itself at the expense of the materials drying, or after being previously heated. This circulation of air goes on continuously. The method adopted in order to maintain a low temperature in the cooling rooms is to allow liquid ammonia, carbon dioxide, or ether to evaporate at the requisite rate through long coils of metal pipes over the outer surfaces of which the moist air is drawn. The latent heat of the ammonia (or other) vapour is obtained at the expense of the heat of the moist air, which is thereby cooled; the vapour condenses on the pipes and the water trickles down into troughs and flows away. The ammonia (or other) gas is repeatedly used in a cycle of operations, being successively liquefied and evaporated. This process is highly efficient, but requires careful handling for economical working.

B. **Mechanical drying.** These methods are efficient when water forms a large proportion of the total weight, and when the solid material to be separated is porous in texture. They leave the solid damp or moist.

Drying by pressure.—There are very few cases in which direct mechanical pressure is used for removing water from substances, the most important of which is the direct squeezing of peat in specially designed machines, in order partly to remove the surplus water.

Filter presses are used for partly drying semi-solids, and leave them still containing about 20 p.c. of moisture. They are efficient in removing the large bulk of the water from granular substances in a state of thick mud. Essentially a filter press consists of a number of flat sections or chambers formed of iron plates covered with filtering cloths, and supported in a strong horizontal frame, in which they can be squeezed up tightly together. The chambers are made either round or square, and usually each has its own outlet cock, while the washing arrangement can be made reversible. The sludge to be filtered is fed in under moderate pressure, and all the outlet cocks opened. After water has ceased to flow out, the solid in the press is washed, if desirable, and the press then taken to pieces to remove the moist solid cakes from its interior. This process is used for filtering,

among other things, sewage sludge, gold slimes, and precipitated pigments.

Drying by centrifugal force.—This method is largely employed for drying clothes in laundries, when the centrifugal machines are termed hydro-extractors. It is also used for drying wool, cotton yarns, piece goods, &c., after they have left the dye houses, and for separating and drying sugar, gun-cotton, and starch.

The process consists in placing the material to be dried in a basket containing numerous holes, and rotating it in a horizontal plane at a considerable speed. The water is thrown off from the material very effectually, much more effectually than when simple filtration or filtration under moderate pressure is adopted.

A centrifugal machine consists essentially of a circular basket, rotated on a vertical central shaft and enclosed in an outer stationary casing. The circular basket is drum shaped, having an open top to introduce the material and sometimes a valve at the bottom to form an outlet for dried crystals. The periphery is perforated with holes of a suitable size. These baskets are made of steel, bronze, copper, aluminium, silver, or china, as may be suitable, and are lined with rubber, enamel, or lead when dealing with acid liquids. The outer stationary casing serves as a guard in case of accident and as a collector for the water. The successful working of a centrifugal machine depends upon the skill with which the vertical shaft is mounted and driven, since the apparatus must have sufficient freedom when running for the axis to take up the position it requires; otherwise vibrations will rapidly wreck the machine.

C. **Drying by evaporation.** This is by far the most efficient method of drying; indeed, several of the preceding processes are only employed as preliminary steps to the application of this more powerful method.

Drying by evaporation is a process in which the water is removed by first converting it into vapour and then conveying the vapour away. Water always has a tendency to pass into the gaseous state, and is constantly giving off vapour from its free surface. If this process occurs in a closed space, some of the vapour finds its way back into the liquid, and a state of equilibrium is set up when the rate at which vapour is leaving the surface has become equal to the rate at which it is passing back into the liquid. To the state of equilibrium at any particular temperature there corresponds a definite vapour pressure, which is a measure of the tendency of water at that temperature to pass into the gaseous state, and this vapour pressure rapidly increases with rise of temperature. When evaporation takes place in free space, no condition of equilibrium is reached, since, owing to diffusion of the vapour, the rate at which it passes back into the liquid can never equal that at which vapour leaves it. Evaporation therefore goes on until no more liquid remains. From these considerations, it follows that the two main practical principles in drying by evaporation are : (i.) to warm the material and thereby increase the tendency of its contained water to vapourise ; and (ii.) to remove the vapour as it is produced from the neighbourhood of the substance, in order that the evaporation shall proceed continuously.

In applying these principles it is necessary to bear in mind that the rate of drying permissible in any given instance is restricted by (a) the physical and chemical nature of the material, which put a limit to the rate at which heat may be safely applied; and (b) by the cost of drying, since the plant mechanically most sound may not be most economical in practice. It must always be remembered that the nature of the material governs the method of drying to be employed, and must be considered before the question of mechanical efficiency.

The various methods for applying heat and for removing vapour are indicated below, and in order to explain more definitely how these methods are employed in practice, brief descriptions follow of various types of drying installations in actual use, and of the purposes for which they are used.

Application of heat. In the majority of cases hot air is employed for conveying heat to the material, and its use is attended with many advantages. Air, although an extremely poor conductor of heat; the increase in volume resulting from this process naturally tends to disperse this heat and to warm surrounding materials by convection. The mobility of the air enables it to come into intimate contact with the surfaces of materials, thereby supplying the heat necessary to vapourise the moisture. Most important of all, the heated air can be thus supplied in large or small amounts, at any desired rate and at uniform pressure, while any of these factors may be rapidly and easily altered at will.

Of the various *sources of heat*, the cheapest is, of course, solar heat. Owing to its unreliability so far as quantity and continuity are concerned, its direct use is attended by considerable risks. Indirectly, however, it is of great value, in being the primary cause of natural air currents. Drying directly by furnace heat obtained by fuel combustion is economical, but the method is restricted in use to drying those substances which are not sensibly affected by high temperatures. For the commonest method of drying, by means of a warm blast of air, heat is usually supplied by passing the air over the surfaces of radiators. These are simply iron vessels, built to expose as much surface as possible, and through the insides of which steam, hot water, or hot gases are passed. Heat is conducted through the iron to the outer surface, and warms the surrounding air mainly by radiation.

The *dangers* encountered in the application of heat result from the nature of the material, and the factors involved, which are briefly discussed below, naturally affect various materials to very different degrees.

(a) Rate of application of heat Although the amount of heat required to vapourise a definite quantity of water is fixed, yet if this heat be applied at a rate faster than that to which the material can accommodate itself, injury will result, e.g. wet bricks will crack unless the greater part of their water is first driven off at a slow and uniform rate.

(b) Change in power of absorbing heat with loss of water. As a material dries, its heat capacity usually diminishes, and hence the risk of overheating increases as drying progresses.

(c) Uncertainty as to degree of dryness, which is often unavoidable.

(d) Local application of heat. This is the usual cause of distortion and cracking, since most materials shrink as they dry, and local shrinking sets up strain. This makes it advisable to keep wet material from actual contact with the source of heat, and to agitate the material to continually expose fresh surfaces, since evaporation is a purely surface phenomenon.

Methods for removal of vapour. The natural method by which vapour is removed is by means of *air currents*, and, excepting in the case of the vacuum process, this is the method upon which all artificial processes for vapour removal are based.

The ordinary *atmospheric* process for drying utilises the natural movements of the air, e.g. by utilising the action of the wind on floors, pans, gantries, sheds, &c. It requires no motive power, but, being dependent upon varying atmospheric conditions, it is not reliable.

In the *exhaust* process the moisture-laden air is drawn away from the wet material quicker than gravity would perform the removal For this purpose a propeller or fan is usually employed. Since the operation is carried out under slightly reduced pressure, vapourisation proceeds quicker than it otherwise would; on the other hand, the exhaust carries away the heat-bearing medium from the material to be heated, and unless proper control is exercised, this defect may more than counterbalance the increased rate of removal of vapour.

In the *vacuum* process the material is enclosed in an air-tight receptacle, from which the air may be exhausted to any desired extent. Heat is then applied, and the vapour pumped off as fast as it is produced. Considerable experience is necessary in the application of this process, which, properly applied, is highly efficient and rapid.

In the *plenum* process the vapour is removed by supplying sufficient warm air to create an augmentation in air pressure A fan is usually employed for this purpose, and drying must, of course, take place in an enclosed room with regulated egress for the air. This process is usually the best to employ, since it can be maintained strictly under control.

Drying installations. Drying floors. *Natural floors* are not often used, since serious difficulties arise as to heating, handling the material, and removing the vapour. Haymaking affords a good instance of its employment

Artificial floors warmed by the products of combustion from a furnace, by hot gases, or by steam passing in flues or pipes beneath, are a considerable improvement on natural floors. Advantage is taken in constructing them of any convenient sandy or porous ground floor; sand is put down if the natural ground is clayey. These floors are used for drying china clay, calcium phosphate, barytes, chalk, cement, and calcined quartz, materials which are not readily injured by excessive or irregular heating.

Drying gantries or racks. These are employed in order that as much surface as possible may be exposed to air currents. Their construction assumes various forms. According to

circumstances, they may be either skeleton shelves, or racks, or props, &c. Occasionally hot water or steam pipes are used as supporting racks, but their use is to be avoided as uneconomical, and tending to produce uneven drying and distortion.

Such substances as damp corn, peat, raw rubber, chalk, bricks, and clayware are frequently dried on open racks, while pigments in colour works are often dried in open gantries of skeleton shelves.

Drying sheds. These are merely drying floors or gantries provided with roofs to keep off rain and snow. These sheds are best constructed of light open framing in order to facilitate the removal of vapour, and the more open it is on all sides the better, provided that the substance is not such that direct sunlight must be excluded from it, e.g. rubber. Such sheds are highly efficient in producing 'air-dried' materials. Bricks are often dried in sheds erected on drying floors, while Chile saltpetre is dried in sheds without the application of artificial heat, as also are china clay and ochre in the quarry state.

Drying pans and troughs. Drying pans, correctly designed and handled, are very useful appliances. The oldest commercial use of such pans is in the evaporation of salt brine, which, as usually carried out, is not at all an economical process. The pans are usually rectangular, and each stands in its own shed. They are directly heated, three or four fires being beneath each pan.

Shallow earthenware pans are of great use in the colour trade, the pigments being readily dried if the pans are carefully arranged on gantries in well-heated and ventilated chambers.

Semi-cylindrical iron pans heated from below by gas or steam give good results in drying soft materials, especially powders. They are most efficient when provided with revolving grids for mechanically stirring the wet material and with valve outlets at the bottom for automatically discharging their dried contents.

Granulated sugar is dried in a type of troughed pan, through which passes a hollow conveyer' carrying hollow paddles. Steam is blown through the conveyer and paddles. The trough is jacketed on one side, and through this jacket air is blown into the bottom of the trough. The sugar is fed into the hot end, and automatically carried by the heated paddles to the outlet at the cool end of the trough.

Kilns. These are buildings containing a furnace, the direct heat of which is used for drying materials by allowing the products of combustion to pass through them. For substances which may be strongly heated without damage, kiln-drying is an economical method of procedure, since the walls of the kiln are very effective in saving heat that would otherwise be lost; but care must be taken to provide proper exits for the vapour.

A primitive type of kiln is one in which calcium phosphate is dried. It consists of a plain rectangular brick building with a wooden roof. The floor is piled with wood, and the phosphate placed upon it. Flues admit air for combustion and circulation. Such a kiln will burn for from 2 to 5 days and dry from 1000 to 1200 tons of phosphate.

Kilns for drying clays, fuller's earth, barytes, and chalk are constructed upon the same principle, the fire being placed so as to prevent the ashes mixing with the material; the latter is sometimes supported within the kiln on iron racks.

A rotating bed dryer is in extensive use for drying materials which allow of direct firing. The material is placed on a circular cast-iron bed, which slowly rotates on a vertical shaft. The bed is covered by a firebrick arch, into which the exit flue leads. Heating is done directly by fires, and stationary blades fixed in the arch stir the material as it is drying. The blades are fixed at such an angle that the material is slowly moved from the centre, above which the feed is situated, to the edge, where it is automatically discharged. This is a common type of drying kiln for ores.

Drying cylinders. This term includes those dryers in which the material to be dried is contained in a cylindrical tube, which is slowly rotated. The essential feature of their construction is that the rotation of the cylinder affords the means of moving the material along. With suitable materials and the necessary power, cylinders will automatically deliver large quantities of uniformly dried product, with the minimum of labour and fuel consumption. They are consequently extensively used, and many types of drying cylinders have been devised.

For materials that withstand high temperatures, the heating may be carried out by passing the hot gases from a furnace through the tube. The latter is constructed of steel, and is mounted nearly horizontally (slope of 1 in 12), with the furnace at the lower end. The feed is situated at the higher cold end, and the gases pass out through a flue at this end, connected with a fan or chimney. As the material gravitates down the tube it is dried, and on reaching the lower end, it drops out, quite dry, into trucks. A modification of this construction consists in enclosing the steel tube in a horizontal brickwork chamber and heating it externally by passing the furnace gases into this brickwork chamber, whence they pass through a series of external hooded openings into the steel cylinder itself. This arrangement allows of a more gradual and systematic heating, while dust and other objectionable parts of the products of combustion may be arrested prior to the gases entering the cylinders. Besides these two arrangements, many others have been devised, each having its particular advantages.

Cylinder dryers are very suitable for heating by steam, thus meeting the requirements of such substances as sugar, salt, soda, cocoa, coffee, &c., provided they contain not more than 25–30 p.c. of moisture. The drying cylinder may be either steam-jacketed externally, or internally, or by both methods united. The exhaust is best taken by means of a fan at the feed end of the cylinder. In using such dryers for sugar, they are employed in conjunction with a conveyer trough dryer (v. supra), into which the sugar falls after passing through the steam-heated cylinder.

Drying rollers. These are heated rotating cylinders, with the outside periphery of which the material to be dried is brought into contact. They are made of steel, cast iron, copper, or

tinned iron, and are usually heated by passing steam or hot air through their interior. Another method of heating consists in coating the cylinder externally with felt and rotating it in a polished iron bed, against the under surface of which steam is blown. The material to be dried is automatically passed between the roller and its bed, and the rollers are usually arranged in series of two to eight.

The latter method is largely employed in laundry work, and the use of drying rollers is extensive in the paper and textile trades.

Drying tunnels. These consist essentially of a stationary passage through which the material passes either continuously or intermittently as the drying proceeds. Drying in a tunnel is progressive from one end to the other. Heat may be applied either by direct firing or by heated air, which passes into the tunnel from beneath one end and travels along to the other. The warm air current usually travels in the opposite direction to that in which the material moves, but not always, as, for instance, in the drying of wool, where the pressure of the warm blast is utilised in blowing the material forward. The vapour-laden air may be removed either by chimney, exhaust, or by pressure fan, while the material may be handled in a very large number of ways, according to circumstances. This method of drying is economical, but the initial cost of plant is often considerable.

In drying timber, the material is carried on special trucks running on a tram track. The air is heated by means of a heater coil fed with steam and situated under the track at the discharging end. The air ascends, dries the timber, thereby becoming cooler and denser, and then, pressed forward by the incoming air, it gravitates into a large space beneath the feeding end of the tunnel and passes up the flue. Wool is dried in a tubular tunnel, being blown along by the warm air. Soap is dried by passing it on trolleys through narrow tunnels, usually arranged in fours, through which warm air is driven by means of a propeller. In particular, bricks and clayware are dried by passing them through drying tunnels, for which purpose a very large number of types of plant have been devised.

Drying rooms. These are enclosed spaces, which are warmed by means of hot air, and into which the loader or discharger has to enter. When not constructed of brick or stone, the material of the walls should be chosen for its insulating qualities.

The expense attached to drying by this method is due largely to the manual labour required in handling the material, which arises, in most cases, from the fact that the peculiar properties of the material render it impossible to utilise mechanical methods. Since manual labour in a heavily moisture-laden atmosphere is unhealthy, desiccation in drying rooms is restricted in practice to those materials for which the process is unavoidable. Such products as hops, confectionery, leather, paper, textile fabrics, pottery, and rubber are dealt with by this method.

The materials are supported in the most convenient manner within the chambers, and warm air circulated either through or over them. The warming of the air may be accom-plished either within or without the compartment, by means of radiators, and, if desired, the same air can be used continuously in a circuit (compare the condensation process).

Drying ovens. These are entirely enclosed drying chambers; the necessary heat for the purpose is not generated within them, neither is it necessary to enter them in order to charge or remove the material to be dried. Ovens can be adapted to suit a wide range of conditions, and some of the most scientific and economical dryers are of this type.

A great variety of methods are available for the purpose of heating, since the heat is generated outside the oven. Products of combustion are readily excluded from the material. There is no necessity for the plant to cool down before the dried product is removed, and hence heat losses are greatly minimised. Heat is applied to the material either by means of hot gases, usually hot air, or by direct conduction through metallic plates, as, for instance, in steam ovens. Vapour is usually removed mechanically, either by pressure or exhaust, but it may be pumped off, as, for instance, in all vacuum machines. Ovens are more efficient than drying rooms, since the latter are frequently used for other purposes than drying, whereas the former are designed exclusively for drying. Only a few types of drying ovens can be here described.

Laboratory ovens are rectangular boxes, constructed of copper, iron, or aluminium, which may be either steam- or air-jacketed, or in simple ovens not jacketed at all. The substances to be dried are supported on shelves inside. With air ovens heat is applied directly at the bottom of the oven or of the outer jacket. A ventilator situated at the bottom of the oven door allows air to enter, and one or more chimneys in the lid allow the warm vapour-laden air to escape. A convenient method of heating, which can be readily controlled, consists in heating electrically, by passing a current through a number of resistance coils embedded in the jacket surrounding the oven. (See also ANALYSIS, Vol. I.) Removable tray dryers are largely used for drying tea, coffee, cocoa, cinchona bark, &c. The trays are arranged in the oven in a series of rows. Each tray has a separate slide, and is independent of the others, and each column of trays has its own regulating damper in the hot air. The method of working is progressive, the wet material being first placed in the top tray of the column and passed downwards stepwise to the bottom. The heat required is supplied from a multitubular furnace, which also produces the air current which aërates the material. The hot air may be allowed to rise through the material, or be drawn down by two centrifugal fans on either side of the centre through the substance. The latter arrangement is more readily controlled, gives a larger output, and effects a considerable saving in height. A modification giving an even larger output consists in causing each horizontal line of trays, commencing with the lowest, to automatically tilt and discharge its contents into the base of the dryer. For drying other substances than those mentioned above, many other types of tray ovens have been devised.

Sliding-panel dryers are used in laundries, and can also be adapted for drying yarns, piece goods, &c. They consist of a row of vertical

sliding panels, built up with hanging rods to form rigid horses for the goods. They are readily movable on runner wheels, and each panel may be withdrawn independently of the others, with the minimum loss of heat, as the back of the panel closes the outlet and thus reshuts the oven. A hot-air blast is supplied from above, and after passing through the oven it discharges into the open.

The Lennox plate-oven dryer is a type which has many advantages, is compact, and occupies a small floor space. The outer vertical cylindrical casing is built up in sections to allow for extension and renewal. A concentric cylindrical drum slowly rotates inside. At each external section there is a horizontal metal plate within the apparatus, and each section plate contains a hole ; these holes are not vertically above one another. The material to be dried is fed in at the top, falls on the first section plate, and is slowly stirred round by horizontal arms on the rotating centre drum till it reaches the hole in the plate. It then falls through on to the next plate, is slowly stirred round till it falls on to the third plate, and so on, till it is discharged at the base. Hot air is blown in at the base, and passes upwards into the central drum, from which it issues, through numerous holes in its sides, passes through the material, and thence upwards and outwards.

A horizontal steam-jacketed cylindrical oven, containing a very powerful and thorough agitating gear inside, is used for drying wet pasty materials like meat, fish, &c. The material is fed in at the top, and discharged as a dry, mealy powder through a manhole in the bottom. The vapour is removed from the interior through a large outlet duct operated either by a fan or pump according to circumstances. In vacuum ovens the removal of vapour by means of air or other gases in motion is discarded in favour of pumping away the vapour from the warmed-up material, operating in a closed space and diminishing the pressure within it to any desired extent. The oven must be strongly built, and all joints must fit tightly to maintain the diminished pressure. The material may be supported inside in any suitable manner, for instance, on steam-heated grids. The necessary accessories are a vacuum pump, a condenser for the vapour and a receiver for the condensed water. The latter is provided with a sight glass in order to tell when no more water is given off by the material in the oven. The effective working of such a plant depends largely upon the observance of various mechanical and engineering points ; the chief feature of the vacuum process is the saving of time that it effects. The oven may be designed to suit either solids or liquids, and provision may also be made for effectively stirring the material during the drying process.

Desiccators. (Laboratory desiccators have already been described.)

A large-scale desiccator is any type of drying machine, which, working by evaporation, carries the degree of drying to the utmost possible extent. In some of the types previously described, it is difficult to prevent thorough desiccation, and, in fact, to avoid dehydration and calcination, but a number of machines have been devised for the effective desiccation of liquids and thin pastes, which work upon a common principle that may be briefly explained. It consists in spreading the liquid in a thin film over a heated metallic surface kept in motion, and, when the water has been removed, skimming off the solid residue with a knife. By suitable arrangements, this process can be made continuous, and it is employed on a large scale for desiccating milk to a dry powder. A modified method of removing the desiccated product is to cause the liquid to spread out on the upper part of an endless horizontal metallic belt, working over two rollers contained in a heated chamber under reduced pressure. The heated liquid, being fed on to the belt at one roller, is desiccated by the time it arrives at the other, and, on the belt passing over that roller, the dry powder falls into the delivery hopper beneath.

Literature.—Marlow's Drying Machinery and Practice, which contains a bibliography of the subject. *See* also a paper by E. A. Alliott, J. Soc. Chem. Ind. 1919, 38, 173 T.

DESICHTOL. Trade name for ichthyol ammonia deodorised by hydrogen peroxide.

DESOXYCHOLEIC ACID *v.* CHOLIC ACID.

DESPYRIN. Salicyl tartaric ester.

DETONAL. Diethyl acetyl urethane.

DETONATORS *v.* EXPLOSIVES.

DEVARDA'S ALLOY. An alloy of aluminium 45, copper 50, and zinc 5 parts.

DEVELOPED COLOURS. Colours formed on the fibre by coupling an azo dye after fixing with a second component. *V.* PRIMULINE.

DEXTRAN *v.* GUMS.

DEXTRINS $n(C_6H_{10}O_5)$. When diastase acts on starch paste (gelatinised starch), maltose is the final product, but, intermediate between the starch and maltose, various dextrins are formed as the reaction proceeds in successive stages. These dextrins are colloidal amorphous compounds, and do not form characteristic derivatives. They are soluble in water, and precipitated by alcohol. Only maltodextrin, which is possibly the simplest of them, has been prepared in anything like a state of purity, and most of the other dextrins described must be regarded as mixtures.

As diastatic hydrolysis proceeds, the optical rotatory power diminishes, and the cupric-reducing power increases. The change is rapid to a certain point, but then becomes arrested ; this behaviour is interpreted as proof of an essential difference between the higher and lower dextrins. The constants of this stage of hydrolysis are $[\alpha]_j = 162.5°$, K (cupric-reducing power) = 48.3, and correspond to the conversion of four-fifths of the starch into maltose. The remaining dextrin is hydrolysed with greater difficulty. According to H. Brown, it cannot have a simpler formula than $40(C_6H_{10}O_5)H_2O$.

The dextrin isolated from a starch conversion stopped at a stage which gives a deep brownish-red colouration with iodine is termed *erythrodextrin*. At a later stage iodine ceases to give a colouration, and the dextrin present is termed *achrodextrin*. These dextrins have little or no cupric-reducing action, this point being still undecided.

Dextrins are also formed by the action of hot dilute mineral acids, or of heat alone on starch. The final product in this case is dextrose instead

of maltose. These methods are used for the commercial preparation of dextrin.

Malfitano and Moschkoff (Compt. rend. 1912, 154, 443–446) have found that starch may be converted into dextrin merely by desiccation. When kept *in vacuo* at 25° over phosphoric oxide 28·1 p.c. of the starch was found to have become soluble in the course of 20 days. The authors conclude that the starch molecule is composed of dextrin complexes linked together by water molecules.

Oscar von Friedrichs (Arkiv. Kem. Min. Geol. 1913, 5, No. 3, 1–14) has studied the action of various yeasts upon the dextrins. Generally speaking, dextrins with higher molecular weights are not so readily attacked as those with lower.

Yeasts which split up α-methyl glucoside are capable of fermenting dextrins to a very limited extent, while *Sacchsia Suaveolens*, which is known to ferment β-methyl glucoside, is found to ferment achroodextrins energetically. The results support the view that β-glucoside linkings are present in the starch and dextrin molecules.

Crystalline dextrins may be prepared by the action of *Bacillus macerans* upon starches (Schardinger, Centr. Bakt. Par. 1911, ii. 29, 188–197). By this method two dextrins designated as α and β have been isolated, both in crystalline form.

According to Langhans (Ber. 1912, 45, 2533–2546), both forms are acetylated by acetic anhydride in presence of zinc chloride, but scission of the molecules occurs simultaneously; under this treatment the α- compound gives a hexa-acetate of a diamylose, the β- a nona-acetate of a triamylose, hydrolysis of the acetates yields a diamylose and triamylose respectively, both crystalline compounds.

The properties of these crystalline dextrins have been further investigated by Pringsheim and Eissler (Ber. 1913, 46, 2959–2974; *see* D. R. P. 279256, 1913), in which the dextrins are produced by the action of *Bacillus macerans* on starch and isolated by precipitation with light petroleum.

In presence of a little platinum black as catalyst, *l*-glucosan, heated to 180°, undergoes polymerization, and is transformed into a white amorphous substance, which exhibits the characteristic properties of a dextrin and yields dextrose when warmed with dilute sulphuric acid (Pictet, Helv. Chim. Acta, 1918, 1, 226).

Maltodextrin $6(C_6H_{10}O_5)H_2O$ has $[\alpha]_J+193·6°$, $[\alpha]_D+181°$; cupric-reducing power, 42. These figures agree with a mixture of 1 part maltose to 2 parts dextrin; but the facts (1) that it cannot be separated into maltose and dextrin by dialysis, (2) that it is not fermentable by yeasts, (3) that it is completely converted into maltose by diastase, prove maltodextrin to be a definite chemical compound. To prepare it, a starch transformation is carried out at 60°–65°, until $[\alpha]_J=+198°$. The solution is boiled, concentrated to a sp.gr. of 1·06, and the maltose removed by fermentation. The solution is filtered, evaporated to a syrup, and digested with alcohol first of 90 p.c., and then of 85 p.c. This last liquid is decanted hot, and the alcohol distilled off, when maltodextrin remains; it is purified by further treatment with alcohol.

On oxidation of maltodextrin with mercuric oxide, until the cupric - reducing power has disappeared, *maltodextrinic acid* is obtained. This behaviour proves maltodextrin to contain an aldehyde group, but the change goes further than the oxidation of this group to carboxyl (CO_2H), since it splits up the terminal C_{12} group into a C_6 acid residue, which remains attached to the rest of the molecule, and a C_6 residue which is eliminated.

(For a full account of the decomposition products of starch, *v.* STARCH.)

Manufacture. — The commercial products known as solid dextrin, British gum, starch gum, &c, are mixtures containing various dextrins, together with carbohydrates (copper oxide reducing substances). They consist mainly of erythrodextrin, and accordingly give a brown iodine colouration.

They are prepared (1) by the action of heat on dried starch; (2) by the action of heat on acidified dried starch.

The starch is first freed as much as possible from combined water by drying in suitable ovens, and then submitted to a temperature of 212°–275° in rotating sheet-iron drums. The heat is supplied by hot oil, rape oil being fairly generally used, or by direct fire. When the oil-bath is used, the control over the temperature is greatest, and the colour of the product can be varied at will from white to dark brown. When the drums are heated by direct fire, they are made to rotate on slightly inclined axes, the dried starch being fed in at the higher end of the revolving cylinder and the product discharged at the other. Sheet-iron ovens are also used; they are constructed singly or in sets. The heat is supplied by a furnace, the heated air from which is drawn over the top of the ovens. The material is kept continually stirred by flat iron oars. Boxes and trays are also used as converters, and, indeed, the maker has only to consider the variety and quality of product required, and to remember that the drier the starch and the lower the temperature of conversion, the whiter will be the product, and, further, that different starches yield different products, *i.e.* behave differently when submitted to the action of heat, to enable him to construct an apparatus that will suit his requirements. It must also be borne in mind that the conversion takes place more slowly at a low temperature.

The alternative method, in which less heat is required to yield a satisfactory product, is to spray or moisten the starch either with a mixture of dilute nitric and hydrochloric acids, or with each acid singly, or with dilute oxalic acid. The paste is dried and heated at 100°–120° or to 150°, till the transformation is complete, as determined by the iodine test; it must then be arrested promptly.

Payen recommended 1000 lbs. starch to be moistened with 30 gallons water containing 2 lbs. nitric acid (sp.gr. 1·38), the mixture to be well kneaded, made up into balls, and dried in a hot-air chamber; then powdered, spread on brass trays to the depth of 1½–2 inches, and submitted to a temperature of from 110°–120° in a hot-air oven.

The heat method is that which was most commonly used on the Continent, whereas the

use of weak nitric acid found most favour in this country.

The products thus obtained appear in commerce in the form of powders varying in colour from almost white to dark brown, through every shade of light yellow and brown. They are reduced to this state after roasting, by crushing in pans or passing through rollers, and then sifting through a rotating silk screen such as is used in flour mills.

Dextrins prepared from powdered starch are used by textile manufacturers and calico printers as vehicles for colours. They are also used for all kinds of gum, paste, sizings, and in the manufacture of paper boxes, wall paper, and for a variety of other purposes.

For a method of examination of commercial dextrin and related starch products, v. Babington, Tingle, and Watson, J. Soc. Chem. Ind. 1918, 37, 257 T.

On heating dry starch with formic or acetic acids, the starch nucleus is broken down and esters of dextrins are formed, which are soluble in cold water. The proportion of acid fixed depends on the time of treatment. After 15 hours' heating with glacial acetic acid at 90°, the product just ceases to give a blue iodine colouration, and the products of the further heating are soluble in cold water When care is taken to exclude moisture, and the heating is continued for 2 or 3 hours only, using equal weights of starch and glacial acetic acid, an acetylated starch, known commercially as *Feculose,* is obtained. This behaves like starch towards boiling water, but the jelly does not revert on standing. It forms very clear flexible films, and is said to give better results than dextrin as a textile finish (*see* Traquair, J. Soc. Chem. Ind. 1909, 28, 288).

Dextrin syrups find employment in a variety of industries. They are prepared from starch by heating it with hydrochloric or sulphuric acids in precisely the manner already described for dextrose (*v.* CARBOHYDRATES), with the exception that conversion is stopped at a much earlier stage. Thus in the modern American process of manufacture of corn syrup from maize starch, less than 10 minutes' heating is required. The product evaporated to 42°–45° B. forms a colourless viscous syrup, having the composition water, 19 p.c. ; dextrose, 38·5 p.c. ; dextrin, 42·0 p.c. ; ash, 0·5 p.c.

In America corn syrup is used extensively in making confectionery, preserves, and table syrups, being preferable to sugar or cane syrup, as the goods are not likely to grain.

According to Yano (J. Chem. Ind. Tokyo, 1918, 21, 865), dextrin prepared by adding 10 parts dilute nitric acid (5 parts of acid of sp.gr. 1·4 and 95 parts water) to 100 parts of sweet potato starch, drying the resulting paste at about 50°, and heating it for an hour at about 150°, is a suitable substitute for gum arabic as an adhesive.

Dextrin may also be prepared by the action of malt extract on gelatinised starch. E. F. A.

DEXTROFORM. A condensation product of dextrin and formaldehyde.

DEXTROSE *v.* CARBOHYDRATES.

DHAK GUM *v.* KINO.

DHAURA. A gum obtained from *Anogeissus latifolia* (Wall.), It is extensively used in India in calico-printing ; it occurs in clean straw-coloured elongated masses, sometimes honey-coloured or even brown from impurities. As an adhesive gum it is inferior in strength to gum arabic. In India, the reputation of this gum stands high with the calico printers, especially of Lucknow, and it is probable it possesses some specific peculiarity justifying the preference, since it is used with certain dyestuffs, such as with haldi (*Curcuma longa* [Linn.]), whilst gum arabic or ' babul ' is used with madder (*Rubia cordifolia* [Linn.]) (Watts' Economic Products of India).

DHURRIN *v.* GLUCOSIDES.

DIABASE. This name was introduced by the French mineralogist A. Brongniart, in 1807, for those varieties of basalt in which the light and dark minerals, respectively felspar and augite (or as he erroneously supposed, felspar and hornblende), are distinguishable to the unaided eye. As naturally defined by him, the term is therefore synonymous with the diorite of Haüy (1822), whilst with the correction of augite for hornblende it becomes a synonym of the dolerite of Haüy (1822). In the latter sense it is used by some authors at the present time (*v.* DOLERITE). Unfortunately, the term was re-defined by German petrographers, and it came to be applied to the older, or pre-Tertiary, dolerites, which differ from those of more recent date only in showing correspondingly more alteration, with the development of secondary minerals, such as chlorite. In consequence of this, the name ' diabase ' is now applied by most English authors to a partially altered or weathered dolerite. In this sense it has an economic bearing, since rocks of this class, being of wide distribution, are much quarried for road mending. For this purpose the fresher dolerites are somewhat brittle, whilst diabases are tougher and more durable, providing the decomposition has not proceeded too far. There is also a tendency to use the name ' diabase ' in a loose sense, like the popular terms ' greenstone,' ' whinstone,' ' toadstone,' and ' trap-rock.'

L. J. S.

DIABETIN. A trade name for a preparation of lævulose.

DIACETYL *v.* KETONES.

DIACETYLDIOXIME, DIMETHYLGLYOXIME *v.* KETONES.

DIACETYL MORPHINE *v.* OPIUM.

DIAL-CIBA. A trade name for diallyl-barbituric acid.

DIALKYL BARBITURIC ACIDS *v.* PYRIMIDINES.

DIALLAGE. An important rock-forming mineral belonging to the monoclinic series of the pyroxene group. It has the same composition as diopside and hedenbergite,

$$Ca(Mg,Fe)(SiO_3)_2$$
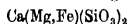
but with the addition of alumina passes into augite. It differs from the other members of the pyroxene group in possessing a fine lamellar structure, due to secondary twinning and partial alteration of the material. On the surfaces of foliation the mineral displays a shining metallic sheen, and on this account it is sometimes used as an ornamental stone. The colour is grey, brown, or green. Diallage is of common occurrence as a constituent of gabbro.

L. J. S.

DIALOGITE. *Manganese carbonate* (v. MAN-GANESE and RHODOCHROSITE).

DIALURIC ACID, *Tartronylurea*

$$CO<^{NH \cdot CO}_{NH \cdot CO}>CH \cdot OH$$
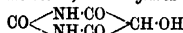
prepared by reducing alloxan with zinc and hydrochloric acid, or with sulphuretted hydrogen at the temperature of boiling water (Liebig and Wöhler, Annalen, 26, 276), or with ammonium sulphide, when ammonium dialurate is obtained and is readily converted into the acid by the action of hot dilute hydrochloric acid (Gregory, Chem. Soc. Mem. 1845, ii. 11). A mixture of potassium dialurate and oxalurate is obtained by adding potassium carbonate to a solution of alloxan containing potassium cyanide (Strecker, Annalen, 113, 53); it is prepared by reducing alloxantin with sodium amalgam, or dibromobarbituric acid with sulphuretted hydrogen (Baeyer, Annalen, 127, 12; 130, 133). Magnier de la Source showed that dialuric acid is obtained by prolonged boiling of uric acid with water (Bull. Soc. chim. 1875, 23, 529), or it can be obtained from uric acid on gentle heating with hydrochloric acid and potassium chlorate (Biltz and Damm, Ber. 1913, 46, 3662-3665). Grimaux effected its synthesis by treating tartronic acid and urea with phosphorus oxychloride (Compt. rend. 1879, 88, 85).

Dialuric acid forms colourless short four-sided prisms, or narrow thin leaflets with rounded ends, sparingly soluble in cold, more readily so in hot water; turns red at 180°, m.p. 214°-215° (corr.) (Biltz and Damm, *l.c.* 3664). The moist crystals or the aqueous solution rapidly absorbs oxygen from the air to form alloxan, which combines with the dialuric acid, forming alloxantin. The rate at which the change takes place is illustrated by the results obtained by Hartley (Chem. Soc. Trans. 1905, 87, 1804), in an unsuccessful attempt to obtain the absorption spectra of dialuric acid; 0·144 gram of pure dialuric acid was dissolved by agitation and warming in 100 c.c. of water, and immediately afterwards the solution yielded the same series of absorption spectra as a solution of 0·322 gram of alloxantin, dissolved in 250 c.c. of water. Alloxantin is also formed by mixing solutions of equivalent quantities of dialuric acid and of alloxan (cf. Richter, Ber. 1911, 44, 2155-2158). Dialuric acid is monobasic, and, contrary to the statements of Menschutkin (Ber. 1875, 8, 760; Annalen, 1876, 182, 70), forms only one series of salts of the type $C_4H_3O_4N_2M'$. The *sodium*, *potassium*, *ammonium*, and *barium* salts are crystalline (Koech, Annalen, 1901, 315; Behrend and Friederich, Annalen, 1906, 344, 1).

Acetyldialuric acid $CO<^{NH \cdot CO}_{NH \cdot CO}>CH \cdot OAc$

crystallises in white prisms or leaflets; m.p. 210°-212°; gives a violet precipitate with barium hydroxide; forms the *potassium salt* $C_6H_6O_6N_2K,H_2O$, and combines with alloxan to form *acetylalloxantin* $C_{10}H_6O_9N_4,H_2O$, m.p. 263°-265°; *benzoyldialuric acid* $C_{11}H_8O_5N_2$, crystallises in prisms, m.p. 209°-210°, yields with barium hydroxide a white precipitate, turning violet, and combines with alloxan to form *benzoylalloxantin* $C_{15}H_{10}O_9N_4,H_2O$, or $1\tfrac{1}{2}H_2O$, m.p. 253°-255° (Behrend and Friederich, Annalen, 1906, 344, 1-18).

Substituted dialuric acids of the type

$$CO<^{NH \cdot CO}_{NH \cdot CO}>C(OH)R$$ are obtained by the

condensation of alloxan with (1) aromatic ketones, *e.g.* phenacyldialuric acid, where $R=C_6H_5 \cdot CO \cdot CH_2-$; (2) aromatic amines, *e.g.* *p*-aminophenyltartronylurea, where

$$R = NH_2 \cdot C_6H_4-;$$
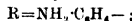
(3) pyrazolone bases, *e.g.* phenylmethylpyrazolonetartronylurea, where

$$R= \begin{matrix} NPh \cdot CO \\ | \\ NMe \cdot CMe \end{matrix} >C-;$$

(4) phenols, *e.g.* *p*-hydroxyphenyltartronylurea, where $R=OH \cdot C_6H_4-$. For the preparation and technical application of these compounds, *see* art. ALLOXAN.

Methyl dialuric acid $C_5H_6O_4N_2 \cdot H_2O$ may be prepared by reducing dimethyl alloxantin with sodium amalgam, crystallises in round clusters of silky needles or narrow lancet-shaped leaflets, m.p. 167°-168° (corr.), or directly from theobromine on careful treatment with finely divided potassium chlorate in presence of hydrochloric acid crystallises in bundles of colourless glistening filaments, many of which widen to slender narrow leaflets. The molecule of water is driven off at 110°-120°. From alcohol the acid crystallises in anhydrous, stout, lustrous rhombohedra, m.p. 184°-185° (Biltz and Damm, Ber. 1913, 46, 3665-3667).

Dimethyldialuric acid

$$CO<^{NMe \cdot CO}_{NMe \cdot CO}>CH \cdot OH$$
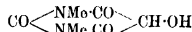
obtained by reducing amalic acid (tetramethylalloxantin) with sulphuretted hydrogen (Maly and Andreasch, Monatsh. 1882, 3, 92), or with sodium amalgam (Techow, Ber. 1894, 27, 3082), forms colourless compact crystals which become red at 100° and decompose at 170° (cf. Biltz and Damm, ibid. 3667-3668); the acid crystallises with one molecule of water, which is partly lost in vacuum and completely at 110°. The hydrated acid has m.p. just under 100°, and decomposes about 210°. The anhydrous acid begins to discolour at 190°, and has m.p. 218° (corr.) with decomposition. It forms crystalline alkali salts, and reduces cold solutions of silver and copper salts.

*iso-***Dialuric acid**

$$CO<^{NH \cdot CH(OH)}_{NH \cdot CO}>C(OH)_2,H_2O$$
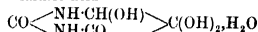
or $CO<^{NH \cdot CH(OH)}_{NH \cdot CO}>CO,2H_2O$, obtained by

the action of bromine water on *iso*-barbituric acid
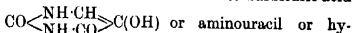
$$CO<^{NH \cdot CH}_{NH \cdot CO}>C(OH)$$ or aminouracil or hy-

droxyxanthine (Behrend and Roosen, Ber. 1888, 21, 999), crystallises in trimetric prisms sometimes a centimetre long (Weinschenk, Annalen, 1889, 251, 243), is readily soluble in water, less so in alcohol; it loses one molecule of water of crystallisation at 100°. The other molecule, which is regarded as water of constitution, is lost at 140°-150°, at which temperature the compound decomposes. *Iso*dialuric acid is converted into dialuric acid by the action of bases (Koech, Annalen, 1901, 315, 246). It yields uric acid on condensation with urea, reduces solutions of silver salts, and combines with hydroxylamine to form two isomeric oximino- compounds. The

2 K

α- oxime forms shining plates or prisms, becomes red and decomposes at 100°; the β- oxime crystallises in needles which do not become red at 110° (Behrend and Roosen, Annalen, 251, 244).

Methylisodialuric acid $C_5H_6O_4N_2$, prepared by oxidising methylisobarbituric acid (Lehmann, Annalen, 1889, 253, 80) with bromine water, crystallises in rosette-like aggregates from water, and in contradistinction to isodialuric acid, contains only 1 molecule of water, which is regarded as water of constitution. M. A. W.

DIAMIDOGEN BLACK, -BLUES v. Azo-COLOURING MATTERS.

DIAMINE BETA BLACK, -BLACK, -BLUE, -BRONZE, -BROWNS, -CUTCH, -FAST RED, -GOLD, -GREEN, -PINK, -ROSE, -SCARLET, -VIOLET, -YELLOW v. Azo- COLOURING MATTERS; PRIMULINE.

DIAMINES v. AMINES.

DIAMINOACRIDYLBENZOIC   ACID v. ACRIDINE DYESTUFFS.

DIAMINOBENZENES, DIAMINOTOLUENES v. AMINES.

4 : 4'-**DIAMINOBENZOPHENONE** v. KETONES.

4 : 4'-**DIAMINODIPHENYL** - 3 : 3' - **DISULPHONIC ACID.** Benzidine disulphonic acid v. DIPHENYL.

2 : 6-**DIAMINOPHENOL-4-SULPHONIC ACID**

$$HO \underset{NH_2}{\overset{NH_2}{\diamondsuit}} SO_3H$$
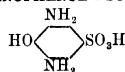
is obtained by reducing a solution of sodium 2 : 6-dinitrophenol-4-sulphonate by zinc dust and hydrochloric acid. Used in the manufacture of azo dyes (Farb. vorm Meister, Lucius, and Brüning, D. R. P. 148212).

DIAMINOSTILBENEDISULPHONIC   ACID

$$NH_2 \diamondsuit \overset{}{CH : CH} \diamondsuit NH_2$$
$$\quad SO_3H \qquad SO_3H$$
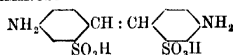
may be prepared by adding zinc dust to sodium p-nitrotoluene sulphonate in a hot solution of caustic soda, until the liquid is decolourised, filtering and acidifying with hydrochloric acid. The precipitated diaminostilbenedisulphonic acid may be purified by re-solution in sodium carbonate, and reprecipitation with acid (Leonhardt and Co. D. R. P. 38735 ; cf. Bender and Schultz, Ber. 1886, 19, 3234). May also be obtained by reducing dinitrostilbenedisulphonic acid with ferrous hydroxide and ammonia (Green and Wahl, Eng. Pat. 5351, 1897 ; Ber. 1897, 30, 3100).

DIAMOND. Carbon crystallised in the cubic system. The contrast presented by the physical characters of the two forms of crystallised carbon—diamond and graphite—is very striking. Diamond is the hardest of minerals, and, indeed, of all known substances, but at the same time it is very brittle ; on the other hand, graphite is one of the softest of minerals, and it is flexible and inelastic. The one is colourless and transparent and a bad conductor of electricity, whilst the other is black and opaque and a good conductor. There is also a considerable difference in density, diamond, 3·52 ; graphite, 2·25. The name diamond, in French and German Diamant, and similar in most other European

languages, is a corruption of the Latin Adamas, which was used for this mineral by Manilius (A.D. 16) and Pliny (A D. 100). This came from Ἀδάμας, meaning invincible, a word applied by the Greeks to hard metals and stones. The similar name adamantine-spar was used by the chemist Joseph Black for corundum. Although diamond and corundum are numbered respectively 10 and 9 in the mineralogist's scale of hardness, and with no other mineral falling between the two, yet, as shown by abrasive tests, diamond is 140 times harder than corundum, and more than a thousand times harder than quartz (No. 7 on the scale). It is on this high degree of hardness that all the technical applications of diamond depend ; and a faceted gem never shows any signs of wear. Lapidaries assert that stones from Borneo and New South Wales are harder than those from other localities.

Crystalline Form.—Crystals of diamond are almost always found singly and with faces developed on all sides ; thus indicating that they grew freely from individual centres in some surrounding medium. By far the commonest form is the regular octahedron, the faces of which are often delicately marked with minute triangular pits or ' etched figures,' whilst the edges are nearly always rounded and often marked with a pronounced furrow. Other forms are a hexakis-octahedron (six-faced octahedron), and less often the rhombic-dodecahedron and the cube, while crystals of distinctly tetrahedral habit are rare. Nevertheless, it is probable that crystals of diamond are really hemihedral (tetrahedral-cubic) ; the apparent octahedron consisting of two tetrahedra interpenetrating in twinned position. Distinctly formed twinned crystals are not uncommon. These are contact-twins with a face of the octahedron as twin-plane, and the two individuals flattened parallel to this plane, giving a triangular plate with re-entrant angles at the three corners. These are known to the Dutch cutters as ' naadsteenen ' (suture-stones). In addition to the rounded edges, noted above, the faces themselves are often curved, sometimes to such an extent that the crystals are almost spherical in form. This rounding, as well as the etched figures, indicate that the crystals have been corroded subsequent to their growth. An important crystallographic character of diamond is the existence of perfect cleavages in four directions parallel to the faces of the octahedron. (On the crystallography of diamond, v. A. Fersmann and V. Goldschmidt, Der Diamant, Heidelberg, 1911).

Physical Characters.—In its optical characters, diamond is remarkable for its very high refractive and dispersive powers, the indices being : for red light (B) 2·40735, yellow (D) 2·41734, violet (H) 2·46476, and the dispersive value (H–B) 0·05741. The critical angles of total reflection corresponding with these indices are 24° 33', 24° 26', and 23° 56', respectively. The angles between the facets of the brilliant form of cutting adopted for the diamond are so arranged that a ray of light entering the gem by the front facet will meet the back facets at a greater angle than the critical angle, and will be internally totally reflected, passing out again from the front of the stone, and with a chance that rays of different colours will be separately

effected. A cut stone, therefore, shows much brilliancy or 'fire,' together with flashes of prismatic colours. Corresponding with the high refractive index, diamond displays a high degree of lustre, which is of the quality known as 'adamantine' lustre. Uncut stones, especially when not quite clear, and with rough rounded surfaces, present a peculiar and very characteristic lead-grey metallic appearance. When pure, diamond is without colour and perfectly transparent. The best stones are described as of the 'first water' or 'blue-whites.' More often there is a tinge of colour ('off-coloured' stones), usually pale yellow, brownish, grey, or greenish. Stones of a good canary-yellow, coffee-brown, or black colour are not uncommon, but those of rich shades of green, blue, or red are very rare. The nature of the colouring matter is uncertain, but it is probably inorganic (e.g. iron and titanium in the brown stones). Changes in colour may be effected by the action of heat or by exposure to radium emanations. Crystals of diamond being cubic, they should be optically isotropic, but when examined under the polarising microscope they are frequently seen to possess anomalous double refraction, especially around enclosures in the stone. This is due to a state of strain, which in some stones is so great that they burst. Phosphorescence is readily produced in diamond by the action of sunlight, ultraviolet, Röntgen, cathode, and radium rays, or simply by rubbing (triboluminescence) Diamond becomes positively electrified by friction. It is very transparent to the Röntgen rays; whilst glass imitations are opaque. Being a good conductor of heat, it can be distinguished from a glass imitation by touching with the tip of the tongue, diamond feeling much colder than glass. The specific heat is less than that of graphite, and it increases rapidly with the temperature.

Chemical Characters.—The combustibility of diamond was first proved experimentally by the Florentine Academicians in 1694. Lavoisier, in 1772, found that the presence of air was necessary, and that 'fixed air' resulted; but it was Smithson Tennant, in 1797, who first proved that equal weights of diamond and carbon yielded equal weights of carbon dioxide More convincing experiments in this direction have been made by Davy, Dumas and Stas, A. Krause (1890), and H. Moissan (1893). Powdered diamond burns readily in air at a red heat. Moissan determined the temperature of ignition in oxygen to be 690°–790°; according to Joly, it is 850° in air. It burns with a small pale-blue flame, and in oxygen is able to support its own combustion. It is infusible even in the electric arc; and it can be heated at high temperatures (1500°) without alteration in various gases (hydrogen, nitrogen, sulphur dioxide and trioxide, and nitrous oxide). In carbon dioxide, however, at 1200° the crystals are corroded, with formation of carbon monoxide. It is unattacked by acids, caustic alkalis, iodic anhydride, hydrogen potassium sulphate, or a mixture of sodium chlorate and nitric acid, but is oxidised when heated to 180°–230° in a mixture of potassium bichromate and sulphuric acid. In fused potassium nitrate or sodium carbonate at about 900° small etched figures are slowly produced; at 1200° the action is more rapid

carbon dioxide being liberated. It is acted upon by sulphur vapour at 900°; and it combines with iron, yielding steel. Crystals are etched by molten olivine (magnesium silicate). The fact that diamond gives with oxidising agents only carbon dioxide, whilst graphite yields graphitic oxide has led to the suggestion that these two forms of carbon are chemical isomerides. Observations at high temperatures are somewhat contradictory; a mere blackening of the surface has often been observed, but not always confirmed. C. Doelter (1911), with crystals packed in charcoal or thorium oxide and heated to 2500°, obtained only a superficial blackening without any alteration in the physical characters of the material. Moissan (1893), however, records the conversion into graphite at the temperature of the electric arc (about 3600°); and Parsons and Swinton (1907) found that a diamond placed in the focus of cathode rays *in vacuô* swelled up into a coke-like mass when the temperature reached 1890°. In this connection the occurrence of cubes of graphite (cliftonite) in meteoric irons is significant; these have been supposed to be paramorphs after diamond.

The ash remaining when diamond is burnt amounts, for colourless crystals, to 0 02–0 05 p c., but in the less pure carbonado it may reach 4·8 p c. It consists mainly of iron oxide and silica, with some lime, magnesia, and titanium. The iron and titanium may represent the colouring matter present in the stone; but the frequent presence of minute enclosures in diamond is not to be overlooked. In addition to liquid enclosures (carbon dioxide and water), the following materials have been recorded: black carbonaceous matter, ilmenite or hæmatite, quartz, rutile, iron-pyrites, gold, chlorite (?), apophyllite, &c.

Varieties.—Differing in certain points from the general characters enumerated above, there are two varieties of diamond—bort and carbonado—which, for technical purposes, are more important than the purer crystals used for gems. These are crystalline aggregates, as distinct from single well-developed crystals

Bort (boart or boort) consists of a number of individual crystals with a radial grouping around a common centre, giving rise to rounded exterior forms These are sometimes quite spherical ('shot-bort'). They are usually rough on the exterior, it being only here that the fibres, or individual crystals, have been free to develop crystal faces—in the interior these have interfered with each other's growth. Although each individual possesses the cleavage characteristic of diamond, yet for the whole mass there is no continuous cleavage. For this reason, bort is tougher than the single crystals, which readily split along the cleavage directions, and is thus better adapted for boring, turning, and cutting tools. This, no doubt, is the explanation of the common statement that bort is harder than diamond; further, since in crystals the degree of hardness varies with the direction, a chance section of bort will present both maximum and minimum values. The rounded pieces of bort are translucent to cloudy and opaque. They are grey or black with a greasy to metallic lustre, and, usually, a peculiar leaden appearance; sp.gr. 3·50. In the trade

the term bort also includes fragments (such as those obtained by bruting), and all crystals and stones that are useless for gem purposes. Such material is of value as an abrasive, but not for tools.

Carbonado, or ' black diamond ' (known in the trade as ' carbon ' or ' carbonate '), is a finely granular crystalline material, dull, black, and opaque, and often more or less porous, with somewhat the appearance of coke. It forms irregularly-shaped masses, and consists of a confused aggregate of minute crystal grains of diamond. It therefore presents no cleavage as a whole, and is consequently tougher and less frangible than crystals. It is less pure than ordinary diamond, yielding more ash (up to 4·8 p.c.) when burnt. An analysis of the ash gave Fe$_2$O$_3$ 53·3, SiO$_2$ 33·1, CaO 13·2 p.c.; MgO trace. The sp gr. is less, 3·15–3·34 (the value for crystals being between the limits 3·516–3·525). The largest known piece of carbonado was found in Bahia, Brazil, in 1895. It weighed 631·9 grams, that is, slightly more than the famous ' Cullinan ' diamond (which weighed 621·2 grams). Both carbonado and bort show considerable variations in texture, and with increasing coarseness of grain they may pass insensibly into ordinary diamond.

Occurrence.—India, from very remote times until the middle of the eighteenth century, was the only source of diamond (with the unimportant exception of Borneo). Since the discovery of the Brazilian and South African deposits the output has gradually fallen off, amounting in 1916 to only 20 carats. The secondary deposits have, however, only been worked by native methods, and the original deposits have not been discovered. Indian diamonds, being of the best gem-quality, there is thus a possibility of further developments. They occur associated with pebbles of jasper and vein-quartz in thin beds of conglomerate in the ancient sedimentary rocks (sandstones and shales) of the Vindhyan system (probably pre-Cambrian), which rest directly on the crystalline rocks. With the weathering of these strata, the diamonds are left on the surface or are accumulated in the alluvial deposits of the present rivers. The districts where mining has been done fall into three main groups : a southern group in the basins of the Pennar, Kistna, and Godavari rivers ; an eastern group in the Mahandi valley ; and a northern group near Panna in Bundelkhand. A doubtful occurrence of diamond in pegmatite has been described from Wajra Karur near Bellary ; and, unfortunately, nothing is known as to whence the diamonds found in the ancient sedimentary rocks were derived. (On Indian diamonds, *v*. Manual of the Geol. of India, vol. 3, Economic Geology, 1881, by V. Ball ; vol. 4, Mineralogy, 1887, by F. R. Mallet.)

In *Brazil*, diamonds were discovered about 1725 in the alluvial gold-washings, at Tejuco (now Diamantina) in Minas Geraaes ; and, although they have been since found in several other districts, notably in Bahia, this has remained the principal diamond-mining centre. Here, as in India, the diamond-bearing alluvial deposits have been derived from conglomerates and sandstones (including the flexible sandstone known as itacolumite) of considerable geological age, and the original rock from which these were derived is not known. The Brazilian deposits are, however, remarkable for the variety of minerals found as well-worn pebbles (' favas ') in association with the diamond ; and the nature of these minerals, or indicators, has led to the suggestion that they, together with the diamonds, originally came from quartz-veins. (On Brazilian diamonds, *see* Mineralogical Papers by O. A. Derby and by E. Hussak ; also E. Hussak, Os Satellites do Diamante, Rio de Janeiro, 1917 ; H. Preston, J. Soc. Arts, 1909, lviii. 101.)

In *South Africa*, diamonds were first discovered in 1867 near Hopetown on the Orange River. In 1868 the important workings (' river diggings ') on the Vaal River were commenced ; and in 1870–1871 the diamonds were traced to deposits of an unique type, in the neighbourhood of which the town of Kimberley in Griqualand West, Cape Province, very quickly sprung up. Here are situated the famous mines De Beers, Kimberley, Dutoitspan, Bultfontein, and Wesselton. Other mines of the same type are the Jagersfontein and Koffyfontein mines in Orange Free State, and the great Premier mine (discovered in 1902) near Pretoria in the Transvaal. The diamond-bearing rock of these mines fills volcanic pipes, 200–300 yards (in the case of the Premier mine half a mile) across, penetrating vertically the surrounding beds of basalt, shale, diabase, and quartzite, and extending to unknown depths. The rock, known as kimberlite, or locally as ' blue ground,' consists mainly of a hydrated magnesium silicate with much the same composition as serpentine. It contains boulders and broken fragments of various rocks (basalt, shale, sandstone, quartzite, granite, mica-schist, eclogite. &c.) and minerals (ilmenite, pyrope, enstatite, chrome-diposide, iron-pyrites, &c.), and is of the nature of a volcanic agglomerate. Diamond is present in this rock on an average of one part in forty millions, and in the richest part of the Kimberley mine one part in two millions. Numerous pipes of a similar character, but containing few or no diamonds, are scattered over a wide area in South Africa. The diamond was brought from below up with the igneous material, which must have been derived from a basic magma rich in olivine. Although the origin of diamond has been the subject of much discussion, there seems no reason to doubt but that it crystallised from this basic magma. The rare presence of diamonds embedded in boulders of eclogite (a garnet-pyroxene rock) found in the blue ground has led to the suggestion that this is the mother-rock ; but it is quite conceivable that the mineral crystallised from more than one kind of basic magma.

The early open workings (' dry diggings ') at the Kimberley mines were soon replaced by a regular system of underground mining. The blue ground, when brought to the surface, is either directly crushed or is spread on floors and exposed to the action of the weather for about a year, when it is crumbly enough to enable the heavy minerals to be separated by washing. From this concentrate the diamonds are separated by means of a mechanical sorting table coated with grease, to which the diamonds adhere, whilst the other minerals pass over. Finally, the stones are cleaned by boiling in a

solution of caustic soda and in aqua regia or hydrofluoric acid. Diamonds also occur in gravels in the Somabula Forest in Southern Rhodesia, and kimberlite pipes have been described as present in this region. In 1908 large numbers of small diamonds were found in the sand-dunes on Lüderitz Bay in South-West Africa; in this case the source of the diamonds have not yet been traced. The output of South African diamonds amounted in 1913 to over five million carats (approximately one ton), valued at 11,389,807*l*. (On South African diamonds, *v.* G. F. Williams, The Diamond Mines of South Africa, 2nd edit. New York, 1907; P. A. Wagner, The Diamond Fields of Southern Africa, Johannesburg, 1914.)

Other diamond-producing countries of less importance are Borneo, New South Wales, and British Guiana. Finds have been reported from many of the states of North America, in British Columbia, Mexico, Dutch Guiana, Russian Lapland, the Ural Mountains, Siberia, China, Western Australia, South Australia, Queensland, Tasmania, Belgian Congo, Gold Coast, and Liberia. In most of these cases the mineral has been found as a few scattered stones in alluvial gold washings. But in Arkansas and British Columbia it has been found in an altered (serpentinised) peridotite of much the same character as the South African ' blue ground.'

The presence of diamond in certain *meteorites* is of special interest. It was first observed in the stone which fell on September 4, 1886, near the village of Novo-Urei on the Alatyr river in Govt. Pensa, Russia. This stone is composed of olivine (67·5 p.c.) and augite (23·8 p.c.), together with nickel-iron, troilite, chromite, black carbonaceous matter, and about 1 p.c. of diamond, the last as minute greyish grains. As dull black grains it has also been found in the meteoric stone of Carcote, Chili. In several, though not in all, of the masses of meteoric iron from Cañon Diablo in Arizona, it has been found as colourless crystals, and as black and colourless grains, the largest 1 mm. across. It is also recorded from the meteoric iron of Magura, Hungary. The cubic form of graphite (cliftonite), probably a pseudomorph after diamond, has been found in the meteoric irons of Youndegin (Western Australia), Smithville (Tennessee), Crosby's Creek (Tennessee), and Magura (Hungary).

Origin and Artificial Production.—The occurrence of diamond in acid igneous rocks and in quartz-veins is very doubtful. On the other hand, its presence in basic igneous rocks is well established ; *e.g.* in kimberlite and eclogite in South Africa, in serpentinised peridotite in Arkansas and British Columbia, and in diabase in New South Wales ; whilst in meteoric stones the matrix is also of the same general character. In these cases the diamond is very probably present as a primary mineral, and one of the first constituents to crystallise out from the basic silicate magma. In addition, we have the occurrence of diamond in the nickel-iron of meteorites. This may be regarded as a magma of a still more basic type, and it is thus probable that diamond may crystallise from basic magmas of widely varying composition.

Many attempts have naturally been made to constrain the abundant element carbon to crystallise as the rare and valuable diamond, but, as yet, with no great measure of success. The results have in many cases been doubtful, and have often not been confirmed. The products are always microscopic and their identification a matter of difficulty. In some cases the very hard carbides of silicon, &c., have probably been mistaken for diamond. The experiments of I. Friedländer (1898), and of R. von Hasslinger (1902–1903), in which carbon was dissolved in molten magnesium silicate (olivine or kimberlite), bear some relation to the natural occurrences, but doubts have been expressed as to whether the microscopic crystals so obtained were really diamond. E. de Boismenu (Fabrication synthétique du diamant, Paris, 1913) states that he obtained crystals up to 2 mm. across by the electrolysis of fused calcium carbide. The only method, however, that has been amply confirmed is that first used by R. S. Marsden (Proc. R. Soc. Edinburgh, 1881, xi. 20) and elaborated by Moissan (1893–1896 ; Le Four électrique, Paris, 1897 ; and The Electric Furnace, London, 1904), in which carbon is dissolved in silver or iron at a high temperature and the mass suddenly cooled by immersion in water or lead. A contracting crust is so formed and the molten interior subjected to great pressure. Sir C. A. Parsons (Bakerian Lecture, Phil. Trans. 1919, A 220, 67 ; and J. Inst. Metals, 1918, xx.) from a long series of experiments, however, concludes that pressure is not a necessary condition, and that the diamond has been formed from gases, probably carbon monoxide, occluded in the iron. O. Ruff (Zeitsch. anorg. Chem. 1917, 99, 73), in a systematic repetition of the various methods, also obtained negative results except by Moissan's method. The presence of microscopic diamonds in certain kinds of hard steel should finally be noted.

Applications.—The value of diamond as a gem depends on its high degree of hardness, enabling it to resist wear, and its high refractive and dispersive power. These optical characters are, however, only brought into full play when the stone is facetted in a particular manner ;
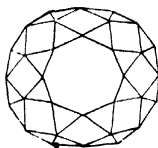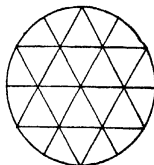
Brilliant-cut.   Rose-cut.
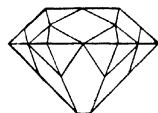
and for this reason, old stones cut by Indian lapidaries have often been re-cut. The form most suited for this purpose is the brilliant-cut, and stones so cut are known as brilliants. The rose-cut, or rosette, is only used for quite small stones usually mounted in number as a surround. The accompanying figures show a brilliant

viewed on the large front facet, or table, and a side-view; and the rose-cut, viewed from above and the side. Being the hardest known material, diamond can only be worked very slowly and tediously with its own powder. The ground-form of the brilliant is approximately an octa-hedron, and this can be obtained, if necessary, by cleavage, or more safely by the modern method of sawing with a thin metal disc charged with diamond dust. The brilliant is then roughly shaped out by rubbing two diamonds together—a process known as bruting. The final grinding and polishing of the facets is performed on a rapidly revolving cast-iron disc fed with diamond dust and olive-oil.

The large historical diamonds with their associations of mystery and romance are mostly of Indian origin; but these are now eclipsed by the numerous, much larger stones found in South Africa. The largest Indian stone still preserved is the 'Koh-i-noor,' which was re-cut in England in 1852 as a brilliant of $106\frac{1}{16}$ carats [1] ($=21\cdot786$ grams). The largest Brazilian stone, the 'Star of the South,' found in 1853, weighed in the rough $254\frac{1}{2}$ 'carats,' and when cut 125 'carats.' The largest known crystal of diamond is the 'Cullinan,' which was found in 1905 in the Premier mine, Transvaal. This showed a large cleavage surface, and was only a portion, probably about half, of the complete crystal. The portion as found weighed $621\cdot2$ grams (3106 metric carats, or nearly 1 lb. 6 ozs. avoir-dupois). Being too large to cut as a single stone, it was cleaved and cut as nine larger gems (weighing from $106\cdot04$ to $0\cdot88$ grams) and ninety-six small brilliants, the yield of cut material amounting to $34\frac{1}{2}$ p.c. The 'Cullinan,' although the largest crystal, is not the largest piece of diamond that has hitherto been dis-covered. A mass of carbonado weighing $631\cdot9$ grams was found in 1895 in Bahia, Brazil.

As an abrasive, diamond powder is the most effective agent available. It is the only material with which diamond itself can be worked, and it is much used by lapidaries for cutting other hard stones. A thin disc of soft iron charged on the edge with diamond powder is used for sawing stones, both for ornamental purposes and in the preparation of thin microscopic sections of rocks. The small steel tools used by engravers of cameos and intaglios, and also the steel points used for boring precious stones, &c., are charged with diamond dust. The material used for abrasive purposes, though included in the trade under the term bort, consists largely of the waste material from shaping the better stones as brilliants, and also the less clear and spotted crystals not suitable for cutting as gems. It is crushed in a diamond-mortar, splinters suitable for other purposes being picked out under a magnifying-glass, and the remainder reduced to a fine powder.

The glazier's diamond is a crystal or frag-ment bounded by two rounded crystal-faces meeting in a curved, or cusped, cutting edge.

[1] This was the old English carat of $205\cdot409$ mg. A later value of the English carat, as defined by the Board of Trade in 1888 and 1889, was $205\cdot304$ mg. The carat-weight has now been standardised in all countries as the *metric carat* of 200 mg. (5 carats = 1 gram). This is the only legal value of the carat in the British Isles since April 1, 1914. *

For writing, drawing, and engraving (*e.g.* fine scales and rulings) on glass, metal, stones, ivory, &c.) fine splinters are used, or the diamond may be cut to a rounded point or chisel-edge. Diamond points are also used for drilling hard stones, glass, porcelain, teeth, &c.

Carbonado and bort, by reason of their absence of cleavage, are much more suitable than ordinary diamond for mounting as small fragments (2–3 carats in weight) as cutting tools which may be subjected to shocks. These are mounted in the crowns of rock-drills, used in tunnelling, mining, and sinking bore-holes for artesian wells, &c.; and on the edges of blade, band, circular, or wire saws for sawing large blocks of marble, granite, &c. Fragments, either in a rough form, or fashioned to a suitable shape, are mounted as lathe tools for working stone, metal, &c. For example, for turning electric-light carbons, the edges of watch-glasses, finishing accurate turning work of the hard steel axles of instruments and machines of pre-cision, boring cannon, forming the sharp-edged furrows on the grinding surfaces of millstones, for dressing emery wheels, &c.

Small cleavage plates or flat crystals of diamond drilled from each side with fine conical holes are used for drawing fine wire, down to $0\cdot01$ mm. in diameter. For the tantalum, tungsten, and osmium filaments of electric lamps the metal is forced by pressure through the hole. Bored diamonds are also used for the pivot-supports of delicate instruments, such as chronometers, electric meters, &c.

The application of diamond for optical purposes is limited by the high cost and difficulty of working. Diamond lenses would need to have a much slighter curvature than those of glass, and they would be immune from scratch-ing. Microscope objectives with such lenses were constructed by Pritchard under the direc-tion of C. R. Goring, in 1824–1826. A hemi-sphere of diamond would also increase consider-ably the range and durability of refractometers.

References.—In addition to the references quoted in the several sections above, the following are given as being of a more general character. M. Bauer, Edelsteinkunde, Leipzig, 1896; 2nd edit. 1909; Eng. transl. (Precious Stones), by L. J. Spencer, London, 1904; C. Hintze, Handbuch der Mineralogie, Leipzig, 1898, vol. i.; C. Doelter, Handbuch der Mineral-chemie, Dresden and Leipzig, 1912, vol. i.; Sir W. Crookes, Diamonds, London, 1909; Sir H. A. Miers, Diamond, article in Encycl. Brit. 11th edit. 1910; E. Boutan, Le Diamant, Paris, 1886; E. W. Streeter, The Great Dia-monds of the World, London, 1882; W. R. Cattelle, The Diamond, London, 1911; Annual Reports on Precious Stones, by G. F. Kunz, The Mineral Industry (New York); and by D. B. Sterrett, in Mineral Resources, United States Geol. Survey.   L. J. S.

DIAMOND BLACKS, -FLAVINE, -GREEN, -YELLOWS v. Azo- COLOURING MATTERS.

DIANA. The alchemistic name for silver.

DIANIL BLACK, -BLUE, -PONCEAU, -YELLOWS v. Azo- COLOURING MATTERS; PRIMULINE.

o-**DIANISIDINE** v. DIPHENYL.

DIANISIDINE BLUE v. Azo- COLOURING MATTERS.

DIANOL BRILLIANT RED, -RED v. AZO-COLOURING MATTERS.

DIANTHINE v. AZO- COLOURING MATTERS.

DIAPHTHERIN, DIAPHTHOL, DIASPIRIN, v. SYNTHETIC DRUGS.

DIARSENAL. Canadian name for salvarsan.

DIASPIRIN. Trade name for succinyl salicylic acid.

DIASPORE. A native hydrated alumina, $Al_2O_3 \cdot H_2O$ or $AlO(OH)$, crystallising in the orthorhombic system and isomorphous with goethite and manganite. It is usually found as scales or foliated masses with a perfect cleavage in one direction on which the lustre is pearly ; but it is readily distinguished from other foliated minerals (mica, &c.) by its much greater hardness (H.$=6\frac{1}{2}$-7). Sp.gr. 3·4. When heated before the blowpipe it decrepitates violently, breaking up into pearly white scales (hence the name diaspore, from διασπείρειν, to scatter). In colour, it is usually grey or yellowish-brown, but pale-violet crystals are also found. It is usually found as an alteration product of corundum and emery, but occurs also as a mineral of contact-metamorphic origin in crystalline limestones. It is of importance as a constituent of bauxite, and in a particular type of bauxite, called diasporite, occurring in crystalline limestone in the Bihar Mountains, Hungary, it constitutes the bulk of the material. L. J. S.

DIASTASE or *Amylase* is the name given to the enzyme or mixture of enzymes which converts starch and glycogen into maltose. In France, the word ' diastase ' is used as a general term for all enzymes, a custom which causes considerable confusion, and which it is to be hoped will lapse.

Diastase is very widely distributed in plants and in animals. It is found in blood serum, in muscle, liver and pancreas, and particularly in the saliva, this latter enzyme being long known under the name *ptyalin*.

The power of germinated barley to hydrolyse starch was discovered by Kirchoff in 1814, and the enzyme preparation was first made by Payen and Persoz in 1833. Diastase is found very generally in the leaves and twigs, in the germinating seeds, in the bark, in the pollen grains, and in the latex of plants. It occurs in yeast and in most of the mould fungi, the enzyme of *Aspergillus oryzæ*, the so-called *Taka diastase* being well known on account of its industrial use in the manufacture of the Japanese beverage, koji.

Diastase, like all other enzymes, has not been prepared in anything approaching a pure state. Considerable uncertainty exists also as to whether it is a single enzyme or a mixture of enzymes acting in turn to convert starch into dextrin and dextrin into maltose. Modern evidence favours the view that it consists of a starch-liquefying enzyme or *amylopectase*, and a saccharifying enzyme able to hydrolyse soluble starch, but without much action on raw starch until this has been rendered soluble by the amylopectase. The two enzymes are found together, but in unequal proportions. Wheaten flour, for example, frequently has a deficiency of liquefying enzyme.

There are well-marked differences between the enzymes present in resting barley and in malt (*cf.* Lintner and Eckhardt, Zeitsch. Ges. Brauw. 1899, 389 ; J. L. Baker, Chem. Soc.

Trans. 1902, 81, 1177), one or the chief of these being that the diastase of raw grain possesses little if any starch-liquefying power. Baker has shown that the products of hydrolysis of starch by alcohol-precipitated enzymes from the two sources, are not the same. Brown and Morris have termed the enzyme of resting barley ' translocation diastase,' that of malt ' secretion diastase ' (Chem. Soc. Trans. 1890, 58, 458 ; 1893, 63, 604). They regarded these as not only different in their actions, but as formed from different materials. This latter assumption has been disputed (*cf.* Ling, J. Inst. Brewing, 1908, 14, 494 ; Ford and Guthrie, *l.c.*, 1908, 14, 61).

Some authors consider the saccharifying enzyme to be a mixture, attributing a different enzyme to each stage in the simplification of the starch molecule. It is impossible at present to make any definite statement on this point. In support of it, it appears that exposure to a temperature of 68° acts more injuriously on the conversion of dextrin to maltose than on that of starch into dextrin. Heating diastase does not affect the liquefying power, though the saccharifying action largely disappears.

The quantity of diastase contained in the barley grain increases gradually in the course of germination : it is said to reach a maximum in about 8 or 9 days, when the plumules are twice as long as the grains.

Diastase as it exists in cereals is partly present as an insoluble zymogen in combination with protein substances which are capable of attack by pepsin ; in solution the enzyme is free and unaltered by pepsin. The dissolved enzyme is more active as the amount of nitrogen in solution increases.

Preparation.—A great variety of methods have been proposed for the preparation of diastase, the majority of these starting from malt. According to O'Sullivan (Chem. Soc. Trans. 1884, 45, 2), finely ground pale barley malt is saturated with water, adding enough to slightly cover it and after 3–4 hours as much of the solution as possible is expressed by means of a filter press. After filtering, alcohol (sp.gr. 0·83) is added, as long as a flocculent precipitate forms, the addition being discontinued as soon as the liquid becomes opalescent or milky. The precipitate is collected, washed with alcohol of increasing strength until dehydrated, pressed between cloth and dried *in vacuo* over sulphuric acid.

Lintner (J. pr. Chem. 34, 378) treats 1 part of green barley malt or flour of air-dried malt with 2 to 4 parts of 20 p.c. alcohol for 24 hours, and precipitates the extract with $2\frac{1}{2}$ volumes of absolute alcohol. The precipitate is washed with alcohol and ether to dehydrate it, and dried *in vacuo*.

Loew extracts germinated barley with 4 p.c. alcohol, and precipitates the extract with basic lead acetate. The precipitate is suspended in water, lead removed with hydrogen sulphide, and the enzyme precipitated with a mixture of alcohol and ether.

Wroblewsky extracts finely powdered malt, first with 70 p.c. and then twice with 45 p.c. alcohol. Alcohol is added to the two last extracts until 70 p.c. is present, the precipitate formed is collected, washed with alcohol and ether, and dried.

For further purification, both Wroblewsky

and Osborne and Campbell dissolve the enzyme in water, and precipitate it with ammonium sulphate, which is added drop by drop, until the liquid contains 50 p.c. On standing, a very active yellowish flaky precipitate is obtained.

Green barley malt may also be extracted with glycerol, and the diastase precipitated by alcohol. Effront extracts with water and induces alcoholic fermentation in the extract so as to remove carbohydrate and protein matter. It is then filtered and the diastase precipitated by alcohol.

Animal diastase is best obtained from saliva. Cohnheim uses freshly prepared calcium phosphate as precipitant, extracts this precipitate with water, and adds alcohol to obtain the enzyme. Alcohol is also used for direct precipitation, likewise ammonium sulphate. Von Wittich extracts pancreas diastase with glycerol.

For the preparation of an active diastatic extract for laboratory use, ground malt should be extracted with twenty times its weight of distilled water at 21° for 3 hours and filtered bright.

The diastase of *Aspergillus oryzae* is sold in commerce as Taka-diastase. A pure form can be prepared from the commercial article by extracting with water, precipitating with ammonium sulphate, dissolving the precipitate in water, dialysing and finally precipitating fractionally with alcohol.

Preparations of diastase obtained as described above are colourless, amorphous, and friable, readily dissolving in water; but if allowed to dry without being dehydrated, they are horny and not easily penetrated by water. They invariably contain ash, which consists of potassium, calcium, and magnesium phosphates, with a trace of sulphate. They give a deep blue colour with a 1 p.c. alcoholic solution of gum guaiacum and hydrogen peroxide.

Lintner's diastase gave the reactions of the proteins, and was found to contain C, 46·66 p.c. ; H, 7·35 p.c. ; N, 10·42 p.c. : S, 1·12 p.c., calculated on the ash-free product. Osborne (Ber. 1898, 31, 254) found for his most active preparation, which had a diastatic power of 600 and contained 0·66 p.c. of ash, C=52·5 p.c., H =6·72 p.c.; N=16·1 p.c., S=1·9 p.c. ; and Wroblewsky gives N=16·5 p.c. for his purest diastase. Both authors regarded diastase as a protein combined, according to Osborne, with a proteose.

The most recent work of Frankel and Hamburg (Beitr. Chem. Physiol. n. Path, 1906, 8, 389) leads to the conclusion that diastase contains neither protein groups nor reducing carbohydrates in its molecule. Impurities were removed from the enzyme solution with lead acetate, the solution sterilised by filtration, and further purified by fermentation with a yeast which had been rendered nitrogen-hungry. This preparation could be divided by dialysis into two distinct enzymes, one of which — the saccharifying—passed through the paper, while the other—the liquefying—was left behind. It showed absence of typical protein reactions, but contained a pentose in small amount.

The purified diastase preparations obtained by Pribram (Biochem. Zeitsch. 1912, 44, 293) from malt extract contained 7·7 p.c. of nitrogen and 1·5 p.c. of ash ; one-sixth of the nitrogenous matter separated as a coagulum on heating. The filtrate on hydrolysis with sulphuric acid

yielded a reducing substance which was considered to be a polycarbohydrate acid which existed in the enzyme in combination with a simple polypeptide. The purified diastase was inactive, but is activated by the addition of traces of lactic acid.

Particularly active preparations have been obtained by Sherman and Schlesinger (J. Amer. Chem. Soc. 1913, 35, 1617) by extracting ground malt with two and a half times its weight of water or very dilute acid phosphate solutions at as low a temperature as possible, with subsequent dialysis, followed by fractional precipitation with alcohol or acetone. The products obtained had a diastatic power of 1800-2200 on the Lintner scale.

The most active preparations contained most nitrogen—about 14 p.c. in maximum. When tested by the Van Slyke method they contained combined nitrogen in all the usual eight forms, the proportions being within the range of variation shown by typical protein substances. The optimum hydrogen ion concentration expressed by Sörensen's exponent was between p_H^+ 4·2 and 4·6 (J. Amer. Chem. Soc. 1915, 37, 623). The purified amylases obtained from the pancreas and from malt are similar in physical properties, show the same qualitative reactions and have the same percentage of nitrogen distributed in the same way among the different types of amino acid radicals (J. Amer. Chem. Soc. 1915, 37, 1305).

The activity of diastase is very greatly influenced by the nature of the substrate on which it acts, more particularly as to whether this is alkaline or acid. Certain substances, such as the amphoteric amino- acids and asparagine, also ammonium and calcium phosphate, increase the activity, asparagine being especially effective in some instances. Vegetable diastase exhibits the maximum activity in presence of traces of weak organic acids. The very smallest quantities of alkali stop action, though this begins again as soon as the alkali is neutralised. In reality, the above accelerating substances are all of acid nature, and the apparently favourable effect of acid is due not to the acid *per se*, but to its neutralising alkaline impurities present. Maximum activity is attained in neutral (in the sense that water is neutral) solution. Minute traces of metallic impurities have an adverse influence. The temperature of maximum activity of diastase is about 55°; heated above this, it begins to show decomposition.

Estimation of diastatic power.—Since it has not been obtained in a pure state, the absolute estimation of diastase is an impossibility ; moreover, the very great influence of external conditions on diastatic activity, to which allusion has been already made, makes it difficult to do more than compare the relative activities of a number of materials under precisely similar conditions. As this is an important operation in brewery control, the methods of analysis have been accurately laid down. The diastatic power is often termed the Lintner value, and expressed in degrees Lintner. The standard is 100° when 0·1 c.c. of a 5 p.c. solution of malt, acting on a 2 p.c. solution of soluble starch for 1 hour at 70°F., produces reducing sugar equivalent to 5 c.c. of Fehling's (Barreswil's) solution.

To obtain accurate results, great stress must be laid on the purity of the distilled water and soluble starch used: commercial starches are frequently alkaline. All work must be carried out in hard-glass apparatus (cf. Ford, J. Soc. Chem. Ind. 1904, 23, 8).

The method adopted by the Malt Analysis Committee of the Institute of Brewing (J. Inst. Brewing, 1906) for malt, is as follows: 25 grams ground malt are extracted with 500 c.c. of distilled water for 30 hours at 70°F. and filtered bright. 3 c.c. is allowed to act on 100 c.c. of 2 p.c. soluble starch at 70°F. for 1 hour. Diastatic action is then stopped by the addition of 10 c.c. N/10-sodium hydroxide, and the liquid made up to 200 c.c. Sugar is then determined either volumetrically or gravimetrically. The results are calculated by the formula

$$\text{Diastatic power} = 1000/xy$$

where x=the number of c.c. of malt extract contained in 100 c.c. of the fully diluted starch-conversion liquid, and y=the number of c.c. of the same liquid required to reduce 5 c.c. of Fehling's solution. When the diastatic capacity exceeds 50°, 2 c.c. or less of malt extract are taken, particularly for the malts over 80° used by distillers and vinegar makers. The diastatic power of English brewing malt ranges between 35° and 40°, that of green malt from 110°–125°, showing that a large proportion of the enzyme is destroyed during the kilning.

Lintner tests solid preparations of the purified enzyme by dissolving 0·2 to 0·5 gram in 50 c.c. water and adding to a series of test-tubes, each containing 10 c.c. of 2 p.c. soluble starch solution, 0·1, 0·2, &c., up to 1 c.c. of the enzyme solution. After an hour, each tube is boiled in the water-bath with 5 c.c. of Fehling's solution, and that determined in which the copper solution is just completely reduced. A second series enables this point to be ascertained with greater accuracy.

Similar methods have been based on the colourations with iodine, shown by starch and dextrin solutions. Wohlgemuth sets increasing quantities of enzyme in a series of tubes with 5 c.c. of a 1 p.c. starch solution under precisely similar conditions. After 30 to 60 minutes at 40°, the tubes are cooled in ice and a drop of N/10 iodine solution added. Colours varying from dark-blue, blue-violet, reddish-yellow, and yellow are obtained. Wohlgemuth selects the tube in which the violet shows as indicating complete conversion to dextrin.

Diastase, like other enzymes which act on carbohydrates, is much affected by the products of its activity with which it forms adsorption compounds—hence the peculiarities exhibited in a starch conversion. Provided that the temperature and other conditions selected are such that the enzyme is not destroyed, the diastase recovered at the end of a reaction is just as active towards a second quantity of starch as an equal portion of fresh enzyme. Diastase is thus a true catalyst (cf. Van Laer, Bull Soc. chim. Belg. 1912, 26, 223).

Uses.—Diastase plays a most important part in the brewing, distilling, and baking industries. Malt extracts, concentrated in vacuo at a low temperature to viscid syrups, are largely used by bread bakers and in some food preparations. Considerable quantities of such active preparations, made from malts of high diastatic power, also find employment in laundries for the purpose of removing starch from stiff collars, shirts, &c. (See also articles STARCH; FERMENTATION; HYDROLYSIS.)   E. F. A.

DIATOMITE (Diatomaceous Earth, Infusorial Earth, Tripolite or Tripoli; Ger. Kieselguhr, Bergmehl). A form of opaline silica consisting of the siliceous remains of diatoms (Diatomaceæ). These are unicellular, free-swimming plants belonging to the large group of Algæ. The cell-wall, or frustule, of each minute individual consists of two shields or valves of siliceous material with elaborate and beautiful ornamentation. More than 10,000 species of diatoms have been described; they vary considerably in form—fusiform, elliptical, discoidal, globular, and acicular. Material composed of individuals of the acicular form, the length of which varies from 0.093 to 0.156 mm. and the thickness 0·00156–0·00468 mm., is best suited for technical purposes. Diatoms multiply extremely rapidly and inhabit both fresh and salt water, being more abundant in cold latitudes. On death, their remains accumulate, under certain conditions, at the bottom of swamps, lakes, or the open ocean. Besides being formed at the present day, such deposits are also met with in strata of Pleistocene and Tertiary age.

Diatomite is a loose, pulverulent material with a mealy or earthy texture, resembling soft chalk or dried clay in appearance. It is friable between the fingers with a harsh feel, and grates between the teeth. In colour it is white, grey, yellowish, brownish, or greenish. It is very light, floating on water; sp.gr. of air-dried material 0·24 and of calcined 0·34. Its high degree of porosity depends on the fact that the shells of the diatoms are hollow. Good material absorbs four or five times its weight of water. Further, it is a bad conductor of heat, electricity, and sound, and is resistant to heat and most chemicals. Of acids, only hydrofluoric attacks it, but it is slowly dissolved by a hot solution of caustic alkali. Chemically it consists of hydrated silica, mixed with various impurities, such as sand, hydroxides of iron, clayey, calcareous, and organic matter. 70–90 p.c. of SiO_2 may be present.

Analysis I, is of white material (dried at 105°) from Auxillac, Cantal, Auvergne; II, of green material from Auxillac; III, from Loch Cuithir (or Quire), Skye, Scotland; IV, from Richmond, Virginia; and V, of Tripolite from Bilin, Bohemia (including also SO_3 0·12, P_2O_5 0·24, NH_4 0·03).

	I.	II.	III.	IV.	V.
SiO_2	91·61	88·56	88·73	75·86	74·20
TiO_2	—	0·10	0·18	—	—
Al_2O_3	—	1·53	2·16	—	9·88	6·81
Fe_2O_3	—	2·22	0·73	0·67	2·02	
CaO	—	0·18	0·26	0·04	0·29	0·41
MgO	—	0·29	0·02	—	—
K_2O	—	trace	0·47	—	1·63	0·02
Na_2O	—	trace	0·44	—	0·30
H_2O	—	2·33	3·01	6·40	8·37	13·30
Organic matter	1·74	4·17	4·15	—	4·20

Tripolite (Ger. Tripel, Polierschiefer=polishing shale) differs from diatomite in being more compact with a laminated structure and consequently less light (sp.gr. 1·86) and porous. It merely represents the same material of a greater geological (Tertiary) age.

The most extensively worked deposits of typical diatomite (Kieselguhr) are those on the Luneburger-Heide (heath) in Hanover. Here beds with a thickness of 10–15 metres occur in basins in Pleistocene sands. The uppermost layers are white, below they are grey, and at the bottom of the deposit green. The green material contains from 15 to 30 p c. of organic matter, sufficient for calcination without addition of fuel. A bed of 5-7 metres covered by Tertiary clay and basalt is worked at Vogelsberg near Altenschlirf in Hesse. Similar deposits of recent to Miocene age are also widely distributed in the volcanic region of central France (Departments of Cantal and Puy-de-Dôme). Here the material is known as *randannite* and *ceyssatite*, from Randanne and Ceyssat respectively; and it is worked commercially under the name *tellurine*. (On the French and German deposits, see C. Schmidt, Ann. des Mines, Paris, 1910, xvij. 370.) Deposits are met with in peat-bogs at several places in Scotland, and beds up to 40 feet in thickness of good quality material are now worked at Loch Cuthir (or Quire) in the parish of Kilmuir in Skye (W. I. Macadam, Min. Mag. 1884, vi 87; 1886, vii. 30, 35; 1889, viii. 135. Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1916, vol. v.). Similar deposits also occur in Co. Antrim (J. H. Pollok, Sci. Proc. R Dublin Soc. 1899, ix. 33). Extensive deposits, many of them of Tertiary age, are of wide distribution in the United States, especially in California, (H. Ries, Economic Geology, New York, 1916). Other localities are Monte Amiata in Tuscany, Victoria,[1] Norway, Denmark, Hungary, Algeria. Chili, &c. The typical tripolite forms yellowish-white bands 0·5-1·5 m. thick in beds of clay, gypsum, and 'Saugschiefer' (absorbent shale) in a Tertiary basin near Bilin in Bohemia.

In the preparation of the material for the market, that of the purer white quality, after being dug out from open pits, is simply air dried in the open or in sheds. Organic matter is removed by calcination. Less pure material, containing sand, &c., is treated by washing and sedimentation. Iron is removed by the action of acids.

The varied uses of diatomite depend 'on its peculiar properties of porosity, lightness, nonconductivity, resistance to heat and acids. It was used by the Greeks and Romans for making light fire-proof tiles; and in the middle ages was mixed with meal for bread, under the impression that it had a medicinal value. As an absorbent it has been much used with nitroglycerine for the manufacture of dynamite. The so-called dry sulphuric acid is prepared by saturating calcined diatomite with three or four times its weight of acid. Such material can be transported with little risk. Diatomite packed around carboys of acid will soak up leakage in case the vessels become cracked. It has also been used as an absorbent of bromine, disinfectants, and liquid manures. On account of its non-conductive properties it is used, sometimes with asbestos, as a light packing material for boilers, steam-pipes, cooking-stoves, safes, refrigerators and refrigerating apparatus, fire-proof and sound-proof floors and partitions of buildings, bulkheads of ships, &c. Mixed with clay, lime, sawdust, &c., it can be used in the manufacture of fire-proof bricks and tiles; and having a low coefficient of expansion such material is specially adapted for making tubes, models, &c. It is used in the manufacture of various cements and artificial stones. Mixed with magnesia cement it gives a fire-proof cement for stoves; with shellac, sealing-wax and gramophone records are made. It is also used as a filtering material for liquids and gases; and various liquids (wine, beer, acids, oil, syrups) can be clarified by stirring with 1 p.c. of diatomite and allowing to settle. As a filler it is employed in the manufacture of rubber, cotton fabrics, paints, safety matches, paper, papier-mâché, soap, scouring-powders, tooth-powders, &c Fused with calcium and magnesium borates it yields a non-cracking glass for glazes and enamels, which can also be used for painting on glass. As a source of silica, it is used in the preparation of sodium silicate, ultramarine, smalt, &c. Finally, as an abrasive (*qv*) it, particularly the tripolite variety, is used for polishing metals and stoves. (*Ref.* B. Dammer and O Tietze, Die Nutzbaren Mineralien, Stuttgart, 1913, vol. i; Diatomaceous Earths (Kieselguhr) and their Utilisation, Bull. Imp. Inst. London, 1905, iii 88–103. L. J. S.

DIAZINE BLACK, -BLUE, -GREEN *v.* Azo-colouring matters.

DIAZO- COMPOUNDS. These organic substances, like the azo- compounds, contain the characteristic group —N_2—, but whereas, in the latter series, this bivalent radical is invariably attached to two carbon atoms, $C·N_2·C$, in the former it is generally, although not invariably combined with only one carbon atom, the other valency being satisfied by (1) an electro-negative ion $\bar{A}c$ in the *diazonium salts* $C·N_2·\bar{A}c$; (2) an oxygen atom in the *diazohydroxides* (' *diazohydrates* ') $C·N_2·OH$ and *diazo-oxides* (' *diazotates* ') $C·N_2·OR$; (3) a nitrogen atom in *diazoamines* (*diazoamino- compounds*)

$$C·N_2·NHR$$

and *diazoimines* (*azimino-compounds*)

$$C·N_2·NH·C;$$

(4) a sulphur atom in *diazosulphonates*

$$C·N_2·SO_3K$$

and *diazosulphides* $C·N_2·S·N_2·C.$

The *diazocyanides* $C·N_2·CN$ contain the azo-group attached to two carbon atoms, one of which belongs to a cyanogen group, and these compounds which, in general, are distinctly coloured, form an intermediate group between the fore-going diazo- derivatives and the azo- compounds.

Certain aliphatic diazo- compounds (*v. infra*) contain the group —N_2— attached by two active valencies to the same carbon atom.

I. Diazonium Salts.

These diazo- derivatives are generally, but not exclusively, prepared from aromatic amines, and the process, which is termed *diazotisation*, is

carried out with the undissociated salt of the amine, and not with the free base. In a hydrolysing solvent like water, it is therefore customary to diazotise aniline and its derivatives with sodium nitrite (1 molecule) and excess (2½ to 3 equivalents) of mineral acid.

AROMATIC DIAZONIUM SALTS.

The diazotisation of the benzenoid and naphthalenoid amines is frequently carried out on a manufacturing scale owing to the employment of aromatic diazonium salts in the production of azo- colouring matters. More than 1000 tons of para-nitraniline are diazotised annually in the production of ' para-nitraniline red '

The aromatic base is dissolved in dilute hydrochloric or sulphuric acid (3 equivalents in 10–20 p.c. aqueous solution) and the solution treated with an equivalent quantity (1 molecule) of sodium nitrite in 10–20 p.c. solution The diazotisation is completed when the liquid contains a slight excess of nitrous acid as indicated by starch and iodide paper.

With aniline and its homologues, the temperature of the diazo- solution is generally maintained at 0°–5° to prevent, so far as possible, the decomposition of the unstable diazonium salt, but in other cases, e g the nitranilines, naphthylamines, benzidine, and other diphenyl bases, the diazotisation is carried out most readily at 10°. The amino anthraquinones are diazotised at 30°–40° (Schaarschmidt, Ber. 1916, 49, 2678).

In the manufacture of soluble azo- dyes, the diazonium salts are generally employed in aqueous solution, but solid diazo- compounds, in dry or paste form, have been introduced to enable dyers to prepare ' ingrain ' azo- colours which are developed on the textile fibres (v Eng. Pat. 18429, 21227, 1894 ; 8989, 11757, 1895 ; 1645, 1896 ; 15353, 1897 ; D R. PP 85387, 88949, 94280, 1894 , 89437, 1896).

In alcoholic or acetic acid solution, diazotisation can be effected on the salt of the amine without using an excess of acid, and ethyl or amyl nitrite may, with advantage, be substituted for sodium nitrite. Gaseous methyl nitrite, which has been employed in certain diazotisation (Chem. Soc. Trans. 1913, 103, 1398), is very readily prepared and is a cleaner reagent than amyl nitrite.

Benzenediazonium chloride $C_6H_5 \cdot N_2Cl$, the simplest example of an aromatic diazonium salt, is prepared by adding the calculated quantity of amyl nitrite to aniline hydrochloride suspended in glacial acetic acid at 10° ; it is precipitated from the clear solution thus obtained by the addition of ether.

Benzenediazonium sulphate $C_6H_5 N_2 \cdot HSO_4$ is prepared in a similar manner from aniline sulphate suspended in glacial acetic acid, the precipitation being effected with alcohol and ether.

Benzenediazonium nitrate $C_6H_5 \cdot N_2 \cdot NO_3$, which was first precipitated from aqueous solution by ether and alcohol (Griess, Annalen, 1866, 137, 39), can be also produced in alcoholic or glacial acetic acid solution (Knoevenagel, Ber. 1890, 23, 2995 ; Bamberger, ibid. 1896, 29, 446 ; Hirsch, ibid, 1897, 30, 92 ; Hantzsch and Jochem, ibid. 1901, 34, 3337).

Diazonium salts have been obtained with a large variety of anions : *platinichlorides, aurichlorides, stannichlorides, ferricyanides, nitroprussiates* (Ber. 1879, 12, 2119, 1885, 18, 965), *chromates* (Jahresberichte, 1867, 915 ; Chem. Soc. Trans. 1905 87, 1), *carbonates* and *nitrites* (ibid, 1905, 87, 921), *fluorides* (Ber. 1903, 36, 2059), *perchlorates* (ibid. 1906, 39, 2713, 3146), *picrates* (Chem. Soc. Trans. 1907, 91, 1316), *azides* (ibid. 1910, 97, 1697 ; Ber. 1903, 36, 2056), *thiosulphates, tungstates* (J. Soc Dyers, 1901, 17, 279), *thioacetates* (Monatsh. 1907, 28,247), *borofluorides* (D. R. P. 281055), *phospho-molybdates* and *tungstates* (Chem. Soc. Trans. 1909, 95, 1319), *arylsulphonates* (Ber. 1911, 44, 1415 , *zincichlorides*, Rev. Gén. Mat Col. 1914, 18, 4 ; *β-naphthol-1-sulphonates*, Eng. Pat. 8989, 11757 of 1895 ; D. R. P 93305.

All diazonium salts are liable to explode in the dry state, for they are endothermic compounds (Berthelot and Vieille, Compt. rend. 1881, 92. 1076 ; Sventoslavsky, Ber. 1910, 43, 1479) and in some cases the explosion point has been determined (Ber. 1899, 32, 1691 ; 1900, 33, 527). The diazonium chromates and perchlorates decompose with considerable violence, so that the former have been suggested as explosives (Bull Soc. chim. 1867, [2] 7, 270 ; Fr. Pat. 73286).

Bisdiazonium salts (*Tetrazo- salts*). These compounds are produced from aromatic diamines which do not contain their aminogroups in *ortho-* or *peri-* positions (v. *Cyclic diazo- compounds*).

When the two amino- groups are in the same aromatic nucleus, complete diazotisation is effected only with some difficulty. Meta-phenylenediamine hydrochloride and sodium nitrite furnish the azo- colouring matters included under the term ' Bismarck brown ' (Ber. 1897, 30, 2111, 2899 ; 1900, 33, 2116), but when a solution of the base in excess of hydrochloric acid is added quickly to a large excess of well-cooled aqueous nitrous acid, complete diazotisation takes place and *benzene-m-bisdiazonium chloride* $C_6H_4[N_2 \cdot Cl]_2$ is produced. When the nitrite is added suddenly to the diamine hydrochloride, nitroso-m-phenylenediamine results. Para-phenylenediamine hydrochloride, when diazotised in the usual way, gives a mixture of diazonium and bisdiazonium chlorides, but when the hydrochloride is added to excess of nitrous acid, *benzene-p-bisdiazonium chloride* is obtained.

In the naphthalene series, 1:4-naphthylenediamine is diazotised with difficulty, owing to its oxidisability, but in producing its azo- derivatives, this difficulty is surmounted by working with its monoacyl- derivatives and diazotising in two stages with an intervening hydrolysis (Eng. Pat. 18783, 1891). The heteronuclear naphthylenediamines, excepting the 1:8- compound, can be completely diazotised, yielding *naphthalenebisdiazonium salts* (Ewer and Pick, D. R. PP. 45549, 45788 ; Badische Anilin und Soda Fabrik. D. R. P. 130475 ; Morgan and Micklethwait, Chem. Soc. Trans. 1910, 97, 2558). Benzidine, tolidine, dianisidine, and other similar heteronuclear diamines of the diphenyl and ditolyl series are readily diazotised, furnishing bisdiazonium salts (e.g. *diphenylbisdiazonium chloride* $Cl \cdot N_2 \cdot C_6H_4 \cdot C_6H_4 \cdot N_2 \cdot Cl$), which are employed in the manufacture of substantive

azo- dyes (v. *Congo red* and *Benzopurpurin* ; art. AZO-COLOURING MATTERS). There are certain substituted para-diamines in the benzene diphenyl and naphthalene series which have hitherto resisted all attempts at complete diazotisation (Ber. 1884, 17, 603 ; 1896, 29, 2285 ; 1905, 38, 3769 ; Eng. Pat. 2946 of 1896).

VELOCITY OF DIAZOTISATION.

Under the usual experimental conditions, diazotisation proceeds with great rapidity, but in N/1000 solutions, the velocity of this reaction has been determined by a colorimetric method for estimating the free nitrous acid. The reaction is of the second order, and the values of the constant $C = \dfrac{x}{t(a-x)}$ are 0·036 for aniline, 0·038 for *p*-toluidine, and 0·041 for *m*-xylidine, with one molecular proportion of free acid at 0°. At higher temperatures, the rate is increased (Hantzsch and Schümann, Ber. 1899, 32, 1691 ; 1900, 33, 527 ; Tassilly, Compt. rend. 1913, 157, 1148 ; 1914, 158, 335, 489). Both colorimetric and electrolytic determinations of the velocity of diazotisation show that, in the absence of disturbing influences, all the aromatic amines are diazotised at the same rate.

ALTERNATIVE METHODS OF PRODUCING AROMATIC DIAZONIUM SALTS.

Nitrosyl chloride or *bromide* has been suggested as a diazotising agent (Tilden and Millar, Chem. Soc. Proc. 1894, 59 ; Kastle and Keiser, Amer. Chem. J. 1895, 17, 91). *Nitrosyl sulphate* has been used with advantage (Pabst and Girard, D. R. P. 6034 ; Ber. 1879, 12, 365 ; Morgan and Micklethwait, Chem. Soc. Trans. 1910, 97, 2558). This reagent or sodium nitrite dissolved in concentrated sulphuric acid is employed in diazotising slightly basic amines (Morgan and Evens, Chem. Soc. Trans. 1919, 116, 1130 ; *cf.* J. pr. Chem 1906, [ii.] 74, 275). *Barium nitrite*, when employed in conjunction with sulphuric acid, furnishes diazo- solutions free from inorganic salts (Witt, Ber. 1903, 36, 4388). The last-named investigator has brought forward an interesting process which consists in dissolving the base in cold concentrated *nitric acid* and adding the calculated amount of *potassium metabisulphite* required to produce sufficient nitrous acid for the diazotisation (Ber. 1909, 42, 2953).

Diazonium bromides are formed by the inter action of *hydrazines* and *diazonium perbromides*

$$2R \cdot N_2Br_3 + RN_2H_3 = 3R \cdot N_2 \cdot Br + 3HBr$$
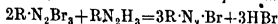
(Chattaway, Chem. Soc. Trans. 1908, 93, 958). An *electrolytic* process for the production of diazonium salts has been patented (Boehringer & Sons, D. R. P. 152926, and Eng. Pat. 2608 of 1904).

Diazonium salts can also be prepared from compounds not containing amino- groups ; mercury diphenyl and nitrous fumes give benzenediazonium nitrate (Ber. 1897, 30, 509), and the same salt is produced from nitrosobenzene and nitric oxide in chloroform solution (*ibid.* 1898, 31, 1528). Fuming nitric acid reverses the coupling process and regenerates the diazonium salt from its azo- derivatives (Meldola, Chem. Soc. Trans. 1889, 55, 608 ; 1894, 65, 841 ; and O. Schmidt, Ber. 1905, 38, 3201).

Diazonium chlorides are regenerated from azo-dyes by decomposing the latter with chlorine or hypochlorous acid (J. pr. Chem. 1912, [ii.] 85, 235.

Certain complex or highly substituted amines resist diazotisation unless treated under pressure (D. R. P. 143450) or with excess of nitrous and mineral acids (Annalen, 1873, 165, 187 ; 1891, 260, 224 ; Ber. 1900, 33, 520).

(For indirect methods of forming diazonium salts, *v.* Annalen, 1879, 199, 320 ; 1888, 243, 282 ; 1892, 270, 116 ; Ber. 1893, 26, 2190 ; 1899, 32, 1809 ; 1900, 33, 1718 ; J. pr. Chem. 1896, [ii.] 54, 496 ; Gazz. chim. ital. 1900, 30, 1526 ; Bull. Soc. chim. 1891, [ii.] 6, 94.)

REACTIONS OF AROMATIC DIAZONIUM SALTS.

In addition to their power of coupling with phenols, aromatic amines, and their sulphonic acids to form the technically important azocolouring matters, the diazonium salts are synthetical agents of the greatest value, and the following is a synopsis of the principal reactions in which they take part :—

1. Decomposition of Diazonium Salts by Water.

(*Cf.* Ber. 1874, 7, 1061 ; 1894, 17, 2704 ; 1899, 32, 1773 ; 1890, 23, 3635 ; 1902, 35, 89 ; J. pr. Chem. 1881, [ii.] 24, 476 ; Chem. Soc. Trans. 1902, 81, 77 ; 1903, 83, 688 ; 1905, 87, 5 ; 1906, 89, 19.)

The decomposition of soluble diazonium salts by water is a unimolecular reaction, and is represented by the well-known equation :

$$C = \frac{1}{t} \log \frac{A}{A-x}$$

The relative stability of the diazonium salts is ascertained by comparing the values of the constant C for a given temperature. The most successful method of making this determination consists in heating solutions of the diazo- compounds at a fixed temperature, and measuring the rate at which nitrogen is evolved. A convenient apparatus, which can be used in this determination and also for studying the decomposition of diazo- compounds in general, is indicated in the following figure.
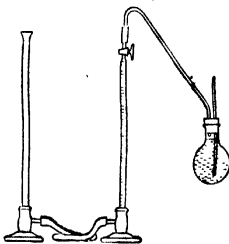
These quantitative decompositions show that the diazonium salts from aniline and ortho- and meta-toluidine are among the least stable of the series, whereas considerably greater stability is exhibited by the diazotised nitranilines and the diazonium sulphonates derived from the benzenoid and naphthalenoid aminesulphonic acids.

The rate of decomposition of diazo- compounds increases with the temperature and in accordance with Arrhenius's formula for the temperature coefficient

$$Cf_1 = Cf_0 e^{A(T_1 - T_0)/T_1 T_0}$$

The rate of decomposition is independent of the quantity of mineral acid present, and equivalent solutions of benzenediazonium chloride, bromide, sulphate, nitrate, and oxalate decompose with the same velocity; this change is, however, accelerated by colloidal platinum or silver, owing to catalytic action (Hantzsch, Ber. 1900, 33, 2517; Hausser and Muller, Bull. Soc. chim. 1892, [iii.] 7, 721; 1893, 9, 353; Compt. rend. 1892, 114, 549, 669, 760, 1438; Schwalbe, Zeitsch. Farb. Ind. 1905, 4, 433; Ber. 1905, 38, 2196, 3071; 1909, 42, 196; Cain, Chem. Soc. Trans. 1902, 81, 1412; 1903, 83, 206, 470; 1905, 38, 2511; Euler, Annalen, 1902, 325, 292; Veley and Cain, Trans. Faraday Soc. 1909, 5, 1).

In general, the decomposition of a diazonium salt by water leads to the formation of a phenol

$$R \cdot N_2 \cdot HSO_4 + H_2O = R \cdot OH + H_2SO_4 + N_2$$
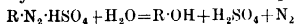
The sulphate is the best salt to employ in this reaction, because the chloride and nitrate are apt to lead respectively to alternative or secondary changes. Benzenediazonium sulphate and its homologues furnish phenol and the cresols and xylenols; diphenyl-4:4'-bis-diazonium sulphate gives rise to 4,4'-dihydroxy-diphenyl. Aurin is similarly obtained from diazotised rosaniline (Annalen, 1878, 194, 306).

In certain cases, more especially in the naphthalene series, the product is contaminated by azo- compounds, resulting from the coupling of the hydroxy- derivative with a portion of the still undecomposed diazonium salt (Chem. Soc. Trans. 1903, 83, 221). To obviate this difficulty, so far as possible, excess of acid is used in the decomposition. The manufacture of the α-naphtholsulphonic acids (e.g. OH : SO₃H = 1 : 4 and 1 : 8) from the corresponding α-naphthyl-aminesulphonic acids furnishes typical examples of the technical application of the process.

Secondary reactions occur even in the simplest cases (Ber. 1890, 23, 3705), and in many instances, where the boiling is protracted owing to the great stability of the diazo- compound, not a trace of the hydroxy- derivative can be isolated (Amer. Chem. Soc. Trans. 1889, 11, 319; Cain, Chem. Soc. Trans. 1903, 83, 688). When the phenolic product is volatile in steam, the normal change is facilitated by operating with solutions boiling above 100°. A good yield of guaiacol is obtained by adding the diazo- salt of ortho-anisidine to a mixture of sodium sulphate and dilute sulphuric acid boiling at 135°–145°, the volatile product being removed at the moment of formation (Kalle & Co., Eng. Pat. 7233 of 1897; cf. Annalen, 1889, 253, 281; Ber. 1874, 7, 1008; D. R. P. 167211; Chem. Soc. Trans. 1906, 87, 19; cf. Willstätter and Schudel, Ber. 1918, 51, 782.

(For other exceptional decompositions of diazo- compounds, v. Ber. 1874, 7, 1061; 1884, 17, 2704; 1899, 32, 1773; 1902, 35, 89; Chem. Soc. Trans. 1896, 69, 1327; 1902, 81, 77, 1905; 87, 5; 1906, 89, 19).

The diazo- compounds are very sensitive to light, which induces the phenolic decomposition

even in certain cases where the action of hot water or acids is very slight (Chem. Soc. Trans. 1907, 91, 35; cf. Compt. rend. 1881, 92, 1074; Ber. 1890, 23, 3131; 1901, 34, 1668; D. R. PP. 53455, 56606; J. Soc. Chem. Ind. 1890, 9, 1001).

2. Decomposition of Diazonium Salts by Alcohols.

The reaction between diazonium salts and alcohols may proceed in two different ways:

1. $R \cdot N_2 \cdot X + C_2 H_5 \cdot OH = R \cdot H + C_2 H_4 O + N_2 + HX$
2. $R \cdot N_2 \cdot X + C_2 H_5 OH = R \cdot O \cdot C_2 H_5 + N_2 + HX$

The former of these changes was originally regarded as the general reaction, but more recent researches have shown that the second is the normal change. The factors determining the course of the reaction are, however, numerous and complicated, involving (1) the nature of the alcohol; (2) the influence of substituents in the diazonium salt; (3) the pressure and temperature at which the decomposition is affected.

The tendency to replace the diazo- group by hydrogen increases with the molecular weight of the alcohol employed. Benzenediazonium chloride or sulphate and methyl alcohol give anisole exclusively. With ethyl alcohol, these salts yield chiefly phenetole, but benzene is also produced. The diazonium sulphates from p-chloro- and p-bromo-aniline furnish only p-chloro- and p-bromo-benzene with ethyl alcohol, but with methyl alcohol they give rise mainly to the methyl ethers of p-chloro- and p-bromo-phenol (Amer. Chem J. 1898, 20, 229; cf. Annalen, 1871, 159, 191; Ber. 1901, 34, 3337; 1903, 36, 2061; Amer. Chem. J. 1893, 15, 518; 1897, 19, 531, 547, 561).

The diazo- salts of the simpler amines (aniline and its homologues) react chiefly in the direction indicated by the second of the foregoing equations, and yield mixed ethers, but the presence of acid substituents

(Cl, Br, NO_2, CO_2H, $NH \cdot SO_2R$)
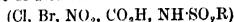
favours the predominance of the first change. The nitranilines (ortho-, meta-, and para-) give respectively 87, 51, and 40 p.c. of nitrobenzene the 1 : 2-, 2 : 1-, and 1 : 4-nitronaphthylamines furnish the corresponding nitronaphthalenes, whereas α- and β- naphthylamines yield α- and β-ethoxynaphthalenes (Remsen and others, Ber. 1885, 18, 65; Amer. Chem. J. 1886, 8, 243; 1887, 9, 587; 1891, 13, 153; 1892, 14, 15).

The yield of alkyl ether increases with rise of pressure, but the addition of zinc-dust or an alkali (sodium hydroxide or ethoxide, potassium carbonate) inhibits almost entirely the formation of mixed ether and leads to the substitution of the diazo- group by hydrogen (Amer. Chem. J. 1893, 15, 105, 301, 320, 379; 1894, 16, 235; 1895, 17, 454; 1897, 19, 163, 531; 1898, 20, 298; 1904, 31, 119).

3. Replacement of the Diazo- Group by Hydrogen.

In addition to the action of alcohol, the diazo- group can be eliminated by the use of a variety of reducing agents :—

(i.) The diazonium salt is reduced to the corresponding *hydrazine* and the hydrazino- group $NH \cdot NH_2$ removed by boiling with *copper sulphate* (Baeyer and Pfitzinger, Ber. 1885, 18, 90, 786).

(ii.) Reduction of the diazo- compound with *alkaline sodium stannite* (Friedländer, Ber. 1889, 22, 587).

(iii) By various other reducing agents, *stannous formate* (Ber. 1885, 18, 357; J. pr. Chem. 1889, [ii.] 40, 97), *hypophosphorous acid* (Ber. 1902, 35, 162), *sodium hyposulphite* (*ibid.* 1907, 40, 858), *formic acid* and *copper powder* (*ibid.* 1890, 23, 1632), *aluminium powder* in alcohol (Morgan and Evens, *l.c.*).

4. Replacement of the Diazo- Group by Halogen, Cyanide, Cyanate, and Thiocyanate Radicals.

Fluorine may be introduced into the aromatic nucleus in place of the diazo- group by treating the diazonium salt with hydrofluoric acid. Diazoamino- compounds (*v. infra*) are also employed in bringing about this replacement, and when treated with concentrated hydrofluoric acid they yield the corresponding fluoro- derivative; fluorobenzene is thus produced from diazoaminobenzene or diazobenzene-piperidide (J. pr. Chem. 1870, [ii.] 1, 395; Ber. 1875, 8, 893; 1879, 12, 581; 1889, 22, 1846).

The first really successful process for replacing the diazo- group by *chlorine* (or *bromine*) was discovered by Sandmeyer, it consists in adding the diazotised solution to cuprous chloride (or bromide) dissolved in warm hydrochloric (or hydrobromic) acid, when nitrogen is evolved and the corresponding chloro- or bromo-derivative is produced (Ber. 1884, 17, 1633, 2650; 1885, 18, 1492, 1496, 1886, 19, 810, 1890, 23, 1628, 1880; Annalen, 1893, 273, 141).

The first stage in the *Sandmeyer reaction* is considered to be the formation of an additive compound of diazonium salt and cuprous chloride; the decomposition of this intermediate product proceeds readily only above a certain temperature, which is different for each diazonium salt (Erdmann, Annalen, 1893, 272, 141; *cf.* Votoček, Chem. Zeit. Rep. 1896, 20, 70; Hantzsch and Blagden, Ber. 1900, 33, 2544). The substitution of bromine for diazo-nitrogen follows a similar course (Phil. Trans. 1864, 154, 673; Annalen, 1866, 137, 49; Amer. Chem. J. 1891, 13, 486; Gazz. chim ital 1890, 20, 631).

The foregoing substitutions are also effected by the addition to solutions of diazonium chlorides or bromides of finely divided copper or the copper bronze of commerce (Gattermann, Ber 1890, 23, 1218; 1892, 25, 1074; Ullmann, *ibid.* 1896, 29, 1878; *cf.* Angeli, *ibid.* 1891, 24, 952).

Iodine is readily substituted for the diazo-complex by treating the acid diazo- solutions with potassium iodide even in the absence of copper or cuprous salts.

The Sandmeyer reaction includes the important synthetical operation of replacing the diazo- group by a *cyanide* radical, the diazonium salt being added to a warm solution of potassium cuprocyanide. The Gattermann process is also applicable to this synthesis, the addition of copper powder to a mixture of diazonium salt and potassium cyanide inducing a similar replacement (Ber. 1890, 23, 1218). The *cyanate* radical is introduced in the place of the diazo- group by adding successively to a solution of diazonium salt, potassium, cyanate, and copper powder (Ber. 1890, 23, 1220; 1892, 25, 1086). The *thiocyanate* group is introduced by adding potassium thiocyanate and cuprous

thiocyanate to a solution of diazonium sulphate (*ibid.* 1890, 23, 738, 770).

5. Replacement of the Diazo- Group by Sulphur and Sulphur-containing Radicals.

These reactions are of importance as furnishing methods for the synthetical production of sulphonic acids.

Thiophenols or *disulphides* are obtained by treating diazonium salts with potassium xanthate and then hydrolysing the resulting aromatic xanthate (Leuckart, J. pr. Chem. 1890, [ii.] 41, 179; *cf.* Ber 1887, 20, 349; Chem. Soc. Proc 1895, 11, 141). Phenyl sulphide is produced by treating benzenediazonium salts with hydrogen sulphide or ammonium sulphide (Ber. 1882, 15, 1683). Benzenoid diazonium salts yield sulphides on treatment with sodium cuprous thio-sulphate, but diazotised α-naphthylamine only gives α-azonaphthalene (Ber 1901, 34, 3968).

The replacement of a diazonium by a *sulphonic* group is effected by saturating with sulphur dioxide an acid solution of diazonium sulphate and adding copper powder; nitrogen is evolved and the resulting sulphinic acid extracted with ether (Gattermann, Ber 1899, 32, 1136; Eng. Pat. 26139 of 1896; D. R. P. 95830).

The foregoing thiophenols, disulphides and sulphinic acids yield the corresponding *sulphonic acids* on oxidation (D. R. P. 70286; Eng. Pat. 11865 of 1892).

6. Replacement of the Diazo- Group by Nitro-, Nitroso-, and Amino- Radicals.

The introduction of a *nitro-* group is brought about either by heating the diazonium salt with nitrous acid and cuprous oxide or by mixing the diazonium sulphate with cupro-cupric sulphite and adding excess of alkali nitrite. By the latter process, 2.4.6-tribromobenzenediazonium sulphate gives 65 p.c. of 1-nitro-2 : 4 : 6-tri-bromobenzene and diazotised β-naphthylamine gives 25 p c of β-nitronaphthalene, a substance prepared with considerable difficulty by other processes (Ber. 1887, 20, 1497; 1900, 33, 2544). The introduction of a *nitroso-* group is effected by treating a diazonium chloride with alkaline potassium ferrocyanide (Ber. 1893, 26, 471). The addition of hydroxylamine to a solution of diazonium salt results in the regeneration of the original amine (Ber. 1892, 25, 372; 1902, 35, 2593, 3920).

7. Formation of Azoimides.

The introduction of the azimino- group N_3 into the aromatic nucleus is effected by the following reactions: (1) action of hydroxyl-amine on diazonium sulphates (Ber. 1892, 25, 372; 1893, 26, 1271; Forster and Fierz, Chem. Soc. Trans. 1907, 91, 855, 1350); (2) interaction of ammonia and diazonium perbromides; (3) direct action of sodium azide on diazonium salts in excess of sulphuric acid (Nölting and Michael, Ber. 1893, 26, 86; Forster and Fierz, Chem. Soc. Trans. 1907, 91, 1942). The last of these processes is carried out so readily that the production of an azimino- compound may be used to estimate the number of diazo- groups in a diazonium salt (Meldola and Hawkins, Chem. Soc. Proc. 1892, 8, 133; Morgan and Mickle-thwait, Chem. Soc. Trans. 1910, 97, 2560). Aromatic azoimides are also produced by the interaction of chloroamine, NH_2Cl, and diazo-nium chlorides (Forster, Chem. Soc. Trans. 1915,

107, 260), and by removing water from the nitrosoarylhydroxylamines.

These aryl azoimides can be employed synthetically as a means of transforming an amine into the corresponding aminophenol when warmed with moderately concentrated sulphuric acid, two-thirds of the nitrogen are eliminated and a hydroxyl group is introduced into the nucleus (Ber. 1894, 27, 192; Morgan and Porter, Chem. Soc. Trans. 1915, 107, 651).

Miscellaneous substitutions, v. Chem. Soc. Trans. 1888, 53, 460; Amer. Chem. J. 1888, 10, 368 ; Ber. 1902, 35, 1964.

For the replacement of the diazo- group by arsinic and stibinic complexes consult ORGANIC ARSENICALS and ORGANIC ANTIMONIALS.

CONDENSATIONS EFFECTED BY MEANS OF AROMATIC DIAZONIUM SALTS.

Azo- compounds are formed, to a slight extent, during the Sandmeyer reaction, and this condensation takes place to a greater extent when the usual order of mixing is reversed and the cuprous chloride added to the cold solution of diazonium salt. Aniline, o-chloraniline, and o- and p-toluidine give considerable quantities of azo- derivatives, but the nitranilines and their homologues furnish diphenyl compounds (Niementowski, Ber. 1901, 34, 3325 ; Ullmann and Forgan, *ibid.* 3802 ; D. R. P. 126961). Cuprous oxide dissolved in ammonia or hydroxylamine also promotes the diphenyl condensation (Annalen, 1902, 320, 122), diphenyl itself being readily prepared by adding copper, zinc, or iron powder to benzenediazonium sulphate in dilute alcohol (Ber. 1890, 23, 1226) ; ββ-dinaphthyl is similarly produced from β-diazonaphthalene sulphate (Chem. Soc. Trans. 1895, 67, 653) 2:2'-Dimethyl-1:1'-dianthraquinonyl results from the condensation of 2 mols. of 2-methylanthraquinone-1-diazonium sulphate when stirred with acetic anhydride and copper bronze powder (Scholl and Kunz, Ber. 1907, 40, 1697; Eng. Pat. 14578 of 1905).

INTERCHANGE OF GROUPS IN DIAZONIUM SALTS.

The diazonium salts of the more highly substituted amines frequently undergo remarkable transformations, some of which have been suggested for use in the technical production of azo- compounds.

The dinitroanisidines, containing nitro- groups either in ortho- or para- positions with regard to the amino- group, exchange these radicals for hydroxyl during the process of diazotisation. In certain instances, the methoxyl group present in these compounds undergoes demethylation, &c., with the production of internal diazo- oxides (quinonediazides). The nitro- group is set free in the form of nitrous acid, which continues the diazotisation process on further quantities of the base (Meldola and others, Chem. Soc. Trans. 1900, 77, 1172 ; 1901, 79, 1076 ; 1902, 81, 988 ; 1905, 87, 1205). Methoxyl or chlorine radicals in para- positions with respect to the diazo-complex are rendered labile by contiguous nitro- groups so that para- diazo-oxides are produced (Klemenc, Ber. 1914, 47, 1407; Morgan and Porter, Chem Soc. Trans. 1915, 107, 653), but an accumulation of acidic (nitro) groups favours the removal of adjacent

nitro- groups and the formation of ortho-diazo-oxides (Meldola and Reverdin, Chem. Soc. Trans. 1910, 97, 1204). A sulphonic group is replaced by hydroxyl in the diazotisation of m-phenylenediaminedisulphonic acid (Eng. Pat. 18283 of 1903), and certain of the dinitronaphthylamines, when diazotised, yield internal diazo-oxides, owing to the initial replacement of a nitro- group by hydroxyl (Ber. 1894, 27, 2211 ; 1895, 28, 1951; cf. Chem. Soc. Trans. 1895, 67, 908).

The replacement of an acidic (electronegative) substituent by hydroxyl frequently occurs on treating the diazonium salt with alkalis.
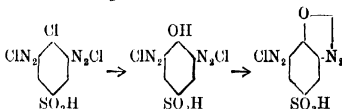
A sulphonic acid group may be similarly eliminated as in β-naphthylamine-1 . 5 : 7-trisulphonic acid which, when diazotised and treated with weak alkali, yields naphthylene-2-diazo-1-oxide-5 . 7-disulphonic acid (D. R. P. 141750 ; Eng. Pats. 16811, 20551, of 1901 ; 1561, 6615, 23993, of 1902 ; 16995, 27372, of 1903 ; 4997, of 1904).

These replacements sometimes take place even when the diazo- solutions are diluted with water, or spontaneously when the diazonium base is present as the salt of a weak acid (acetate, oxalate, carbonate, &c) (v. Orton, Proc. Roy. Soc. 1902, 71, 153 ; Chem. Soc. Trans. 1903, 83, 796 ; 1907, 91, 1554 ; Nolting and Battegay Ber. 1906, 39, 79).

p-Chlorobenzenediazonium thiocyanate

$$Cl \cdot C_6H_4 \cdot N_2 \cdot CNS$$

undergoes a remarkable molecular transformation when dissolved in alcohol containing a trace of hydrochloric acid. The thiocyanate and chlorine radicals change places, and on adding ether to the solution, p-thiocyanobenzene diazonium chloride is precipitated (Hantzsch, Ber. 1896, 29, 947). Similarly, 2 : 4 : 6-tribromobenzenediazonium sulphate in presence of excess of potassium thiocyanate is converted into 2.4:6-trithiocyanobenzenediazonium thiocyanate and many brominated diazonium chlorides pass into chlorinated diazonium bromides (Ber. 1897, 30, 2334 ; 1898, 31, 1253 ; 1900, 33, 505 ; cf. Chem. Soc. Trans. 1902, 81, 1376). The last of these transformations has been studied quantitatively, and the following generalisations have been established :—

(i.) Bromine atoms are replaced by chlorine only when present in the ortho- or para- position with respect to the diazonium group, those in ortho- positions being most readily removed. A bromine atom in the meta- position is not affected.

(ii.) The ease of transformation increases with the number of bromine atoms present.

(iii.) The transformation constant, calculated from the equation for a unimolecular reaction $K = 1/t(\log A/A - x)$, increases with the temperature and is also influenced by the solvent, having its minimum value in water, and becoming greater as the series of alcohols is ascended.

(iv.) Diazonium salts containing two bromine atoms are stable when dry, but are rapidly transformed in ethyl alcohol; 2:4:6-tribromobenzenediazonium chloride becomes transformed in the dry state.

These changes do not occur either with iodinated diazonium chlorides or with brominated diazonium fluorides (Hantzsch, Ber. 1903, 36, 2069).

CONSTITUTION OF AROMATIC DIAZONIUM SALTS.

Aromatic diazonium salts are generally soluble in water to a neutral solution, thus showing, by an absence of hydrolytic dissociation, that the diazonium base is a stronger base than the aromatic amine from which it was derived. The strength of the diazonium base has been confirmed by physico-chemical measurements.

Determinations of the electrical conductivity of solutions of benzenediazonium chloride and nitrate show that the benzenediazonium radical is strictly comparable with other quaternary ammonium ions. The rate of migration of the benzenediazonium ion at 25° is 45·7, the corresponding constants for the methylpyridinium and tetramethylammonium ions being 44·3 and 43·6 respectively. The molecular electrical conductivity of solutions of diazonium salts increases with dilution, just as in the case of the corresponding potassium and ammonium compounds.

The affinity constant of benzenediazonium hydroxide at 0° is 70 times greater than that of ammonium hydroxides, and somewhat exceeds that of piperidine. The affinity constants of p-methoxybenzenediazonium and ψ-cumidinediazonium hydroxides are even greater, and approximate closely to those of the alkali hydroxides. A comparison of the electrical conductivity experiments, with the results obtained in the hydrolysis of ethyl acetate by benzenediazonium hydroxide, shows that in N/128 solutions at 0°, approximately 33 p.c. of the base exists in the ionised condition (Ber. 1890, 23, 3220 ; 1895, 28, 1737 ; 1898, 31, 1612).

Benzenediazonium (Diazobenzene) behaves like an alkali or a complex ammonium cation.

Benzenediazonium hydroxide (Diazobenzene hydrate or hydroxide) is only known in solution, and is produced by treating aqueous benzenediazonium chloride with the calculated amount of silver oxide, or by adding barium hydroxide to a solution of benzenediazonium sulphate (Hantzsch, Ber. 1898, 31, 340). The solution is strongly alkaline, and gives at once an azo-compound with β-naphthol ; the dissolved base decomposes, however, fairly rapidly even at 0°.

The striking similarity in the physical and chemical properties of the diazonium and quaternary ammonium salts suggests the existence of quinquevalent nitrogen in the former compounds, and on these grounds the following formula, formerly proposed by Blomstrand (1869), Strecker (1871), and Erlenmeyer (1874), has now been generally adopted for benzenediazonium chloride and its homologues :

$$\text{C}_6\text{H}_5\text{---N}^\text{V}\text{---Cl}$$
$$\overset{|}{\text{N}}$$
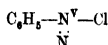
although, for many years, the alternative configuration, $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{Cl}$, suggested by Kekulé, was usually employed.

The close analogy existing between the diazonium and alkali salts is shown further by the facility with which the former yield double salts with cobaltic nitrite and with the chlorides of platinum, gold, and mercury. Diazonium perhalides are also known, corresponding with the perhalides of potassium, rubidium, cæsium, and quaternary ammonium bases (Ber. 1895, 28, 1736, 2754).

The benzenoid diazonium salts with colourless anions (nitrates, sulphates, chlorides) are generally colourless, but the corresponding bromides, iodides, and thiocyanates are coloured, and the deeper the colour the more explosive the salt. When cooled in liquid air, these coloured salts become less coloured ; moreover, their aqueous solutions are colourless.

The development of colour and increase in explosibility are considered by Hantzsch to indicate a change in constitution, the coloured substance being regarded as an equilibrium mixture of diazonium salt and syn-diazocompound (v. infra). This equilibrium is disturbed in the sense of forming more colourless diazonium salt by lowering the temperature or by dissolving the substance in water (Hantzsch, Ber. 1897, 33, 2179 ; 1900, 33, 2179 ; Euler, Ber. 1895, 31, 4168). But although in the benzene series the diazonium chlorides, nitrates, and sulphates are colourless, yet in the diphenyl and naphthalene series, many diazonium salts with these anions are coloured and comparatively stable. Moreover, this colour (yellow or orange) is retained either in aqueous solution or at the temperature of liquid air. Apart from their colour, these salts have all the properties of the simpler diazonium salts (neutral solutions, coupling with phenols, &c.). These facts indicate that increase in the complexity of the organic portion of the diazonium cation leads to the development of colour in normal diazonium salts.

(Coloured diazonium salts, v. Hantzsch, Ber. 1900, 33, 3183 ; 1901, 34, 4168 ; Annalen, 1900, 312, 126 ; Cain, Chem. Soc. Trans. 1905, 87, 5 ; Morgan and others, ibid. 1907, 91, 1311, 1505 ; 1908, 93, 614 ; 1909, 95, 1319.)

The idea embodied in Blomstrand's diazonium formula (v. supra) fails to express one important point, namely, the dependence of the stability of the diazo- complex on the presence of an unsaturated group. Yet this is a matter of fundamental importance, for hitherto no amine in which the basic nitrogen is attached to a fully saturated ring or complex has yielded a diazonium salt.

Cain has suggested an alternative formula, (2), giving expression to this circumstance (Chem. Soc. Trans. 1907, 91, 1051), in which the diazonium salt is represented as having a para-hemiquinonoid constitution ; and this conception has been extended by Morgan (ibid. 1908, 93, 617 ; 1910, 97, 2563) so as to include the equally admissible ortho-hemiquinonoid configurations (1) and (3) :

(1)   (2)   (3)
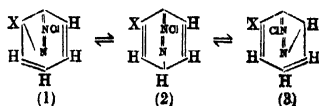
Euler has also advocated a para- hemiquinonoid structure for diazonium salts (Ber. 1908, 41, 3979).

NON-AROMATIC DIAZONIUM SALTS.

The foregoing hypotheses of the constitution of aromatic diazonium salts, which bases their existence on the unsaturated nature of the aromatic complex, accord with the fact that certain non-aromatic primary amines containing unsaturated organic groups manifest, in some degree, the property of diazotisability. Among these bases are aminotriazole (I.) and its derivatives, and aminoantipyrine (II.) :

$$NH_2-C \underset{\underset{N-CH}{\|}}{\overset{NH\cdot N}{<}}$$
I.

$$\overset{N(CH_3)\cdot N(C_6H_5)\cdot CO}{\underset{C(CH_3)---C\cdot NH_2}{|}}$$
II.
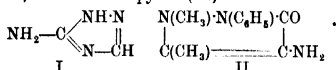
(Thiele and Manchot, Annalen, 1898, 303, 33 : Knorr and Stolz, ibid. 1896, 293, 67 ; cf. Ber. 1900, 33, 1158; 1906, 39, 2925 ; Annalen, 1900, 312, 133). In addition to amino derivatives of the pyrazoline group (Michaelis, Annalen, 1906, 350, 288), the 4- and 5-amino derivatives of the pyrazole group give rise to remarkably stable diazonium salts (Morgan and Reilly, Chem. Soc. Trans. 1914, 105, 436 ; Michaelis and others, Annalen, 1911, 385, 1 ; 1915, 407, 229, 274; Mohr. J. pr. Chem. 1914; [ii.] 90, 569). 2-Aminothiazole, a heterocyclic base containing sulphur and nitrogen in the ring, furnishes diazonium salts of the oxyacids (Morgan and Morrow, Chem. Soc. Trans. 1915, 107 1291). Distinct evidence of diazotisability has been adduced in the indole and pyrrole series (Angeli and d'Angelo, Atti. R. Accad. Lincei, 1904, [v.] 13, i. 258; Angelico, l.c. 1905, 14, ii. 167). It has also been shown ;K. A. Hofmann, Hock and Roth, Ber. 1910, 43, 682, 1087) that aminoguanidine gives rise to diazonium salts, derived, however, not from the salts of aminoguanidine itself, but from a more complex molecule containing two guanidine residues, and having a greater degree of unsaturation. The diazonium nitrate, for example, is represented by the formula :

$$NH \underset{\overset{}{}}{\overset{NO_2\cdot N_2\cdot NH\cdot C(:NH)}{\underset{C(NH_2)\cdot NH-NH\cdot N}{\diagdown}}} N$$
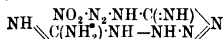
containing a diazo- complex associated with an open chain having three unsaturated linkings.

II. CYCLIC DIAZO- COMPOUNDS.

In certain instances, the action of nitrous acid on substituted aromatic amines leads to the formation of compounds having their diazonitrogen in a cyclic complex, this result being due to the subsequent interaction of a substituent group.

1. INTERNAL DIAZONIUM SALTS.

Sulphonated amines of the benzene and naphthalene series furnish diazo- derivatives which are generally misnamed diazo-sulphonic acids. These compounds, however, do not contain ionic hydrogen, and are really internal diazonium salts ; No. 1, the so-called 'diazobenzenesulphonic acid,' being benzenediazonium-p-sulphonate, whilst No. 2 is naphthalene-1-diazonium- 5-sulphonate
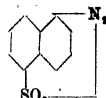
(1.)   (2.)

These internal diazonium sulphonates are of great technical importance in the manufacture of azo- dyes (v. AZO- COLOURING MATTERS). They are prepared either by adding sodium nitrite to an acid suspension of the amino sulphonic acid or by acidifying a solution containing nitrite and the alkali salt of the aminosulphonic acid (Rev. prod. chim. 1917, 20, 21).

Of a similar nature are the cyclic diazo-derivatives obtained by diazotising aromatic aminocarboxylic acids (cf. Bülow and Haas, Ber. 1911, 44, 601), e.g. 'diazo-anthranilic acid' or benzenediazonium-o-carboxylate

which is employed in the production of methyl red (v ACIDIMETRY and ALKALIMETRY).

2. CYCLIC DIAZO- COMPOUNDS DUE TO INTERNAL CONDENSATION.

Aromatic ortho- and peri-diamines do not yield diazonium salts, inasmuch as their interaction with nitrous acid leads at once to the formation of cyclic diazoimines (Azimino-compounds)

(1.)   (2.)

Phenylene-o-diazoimine (1) (Aziminobenzene) and **naphthylene-1:8-diazoimine** (2) (1:8-Azimino-naphthalene) are typical members of this series of diazo- compounds.

The triazole rings thus set up are remarkably stable, and in the case of the ortho- derivatives (No. 1) are not opened by mineral acids without complete rupture of the molecule. The peri-diazoimines (No. 2) occupy a position intermediate between the ortho-diazoimines (No. 1) and the para-diazoimines (v. infra).

The 1:2- and 2:3-naphthylene-diamines furnish respectively 1:2- and 2:3-naphthylene-diazoimines (1:2- and 2:3-aziminonaphthalenes). (Constitution of ortho-diazoimines and their acyl- derivatives, Griess, Ber. 1882, 15, 2195 ; Kekulé, Lehrbuch, ii. 739 ; Morgan and Godden, Chem. Soc. Trans. 1910, 97, 2557 ; cf. Ber. 1874, 7, 316 ; 1876, 9, 221 ; 1887, 20, 2999 ; 1894, 27, 874 ; Annalen, 1889, 255, 344 ; Chem. Soc. Trans. 1906, 89, 4.) Although Griess's formulation for the azimino- compounds

$$C_6H_4 \underset{\overset{}{}}{\overset{N}{\underset{N}{<}}} NH \text{ still persists in chemical litera-}$$
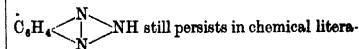
ture, it has been disproved completely, and that of Kekulé substantiated by the preparation of three pairs of isomerides having respectively

2 L

the following formulæ, where R=acetyl, benzoyl, or benzenesulphonyl.
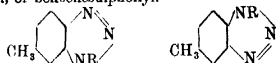
This form of isomerism could not exist with Griess's symmetrical configuration (Morgan, Micklethwait and Scharff, Chem. Soc. Trans. 1913, 103, 1394; 1914, 105, 117). Although these diazoimines do not couple with phenols and aromatic bases to form azo-dyes, yet a synthetic employment has been found for them in the production of carbazole derivatives which are obtained on heating these cyclic diazo-compounds (Ullmann, Ber. 1898, 31, 1697; 1914, 47, 380).

Similar stable cyclic diazo- compounds are obtained by diazotising the ortho-aminothiophenols, o-**phenylenediazosulphide** being a colourless crystalline substance with a sweetish odour and feebly basic properties

$$C_6H_4<^S_N>N$$

(Jacobsen, Annalen, 1893, 277, 209, 218, 232, 237).

3. CYCLIC DIAZO-COMPOUNDS DUE TO COMBINED INTERNAL CONDENSATION AND SALT FORMATION.

In this group are found certain diazo-derivatives of amines containing slightly acidic substituents in ortho- or para-, but not meta-positions with respect to the aminic nitrogen.

(I.) **Internal diazo- oxides** are produced from ortho- and para- aminophenols and their derivatives. In some cases, an intermediate diazonium salt is formed which condenses to the diazo-oxide on treatment with silver oxide or an alkali (Schmitt, Ber. 1868, 1, 67; Hantzsch and Davidson, ibid. 1896, 29, 1522; Cameron, Amer. Chem. J. 1898, 20, 229). The first diazo-compound prepared by Griess (Annalen, 1858, 106, 123), namely, **dinitrobenzenediazo-oxide**.

$$(NO_2)_2C_6H_2<^O_{N_2}>|$$

belongs to this class; it is produced by diazotising picramic acid, and has been utilised in the production of azo- colours (D. R. P. 151332). The 1:2-, 2:1-, 2:3-, and 1:8 aminonaphthols and their sulphonic acids similarly give rise to internal diazo-oxides which are so stable that they can be nitrated. These internal diazo-oxides are readily transformed into diazonium salts by mineral acids, and are therefore available in the production of azo-dyes (Eng. Pat. 28107, of 1897; 10235, 15025, of 1904; Fr. Pat. 353786 of 1905; D. R. PP. 155083, 164665, 171024, 172446, 175593, 176618, 176619, 176620).

Internal diazo-oxides can also be produced by leaving the diazonium salts of highly substituted amines (e.g. 2:4:6-trichloroaniline) in aqueous solutions containing no free mineral acid (Orton, Proc. Roy. Soc. 1903, 71, 153; Chem. Soc. Trans. 1903, 83, 796).

These diazo- derivatives have been formulated either as cyclic diazo-oxides (I.) or as quinonediazides (II.):

$$O\cdot C_6H_4\cdot N_2$$
I.

$$O:C_6H_4<^N_N$$
II.
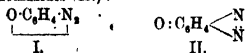
(cf. Wolff, Annalen, 1900, 312, 126; Morgan and Micklethwait, Chem. Soc. Trans. 1908, 93, 607).

Repeated attempts to prepare internal diazo-oxides from m-aminophenol and its nitro-derivatives, which have been quite unsuccessful, strengthen the view that these diazo- derivatives are to be regarded as quinonediazooxides (II.), with the reservation that similar complex compounds are producible from 1:8-aminonaphthol, ' H acid,' and other peri- derivatives (Morgan and Porter, l.c.). In the case of aminophenolsulphonic acids the NH_2:OH=1:2 compounds give these coloured o-quinonediazides; the NH_2:OH=1:4 compounds yield diazonium sulphonates changing to p-quinonediazides on partial neutralisation; the NH_2:OH=1:3 compounds give rise only to diazonium sulphonates which lose diazo-nitrogen and furnish complex azo derivatives on treatment with alkali (Morgan and Tomlins, Chem. Soc. Trans. 1917, 111, 497).

(II.) **Para-diazoimines and diazoimides.**

The simplest example of the para-diazoimines is obtained by the action of alkalis on the diazonium salts of p-aminodiphenylamine (Annalen, 1888, 243, 282; Ber. 1902, 35, 895). The following alternative formulæ (III. and IV.) have been given to this product :—

$$C_6H_5\cdot N\cdot C_6H_4\cdot N_2$$
III.

$$C_6H_5N:C_6H_4<^N_N$$
IV.
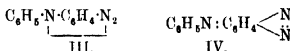
corresponding respectively with the foregoing formulæ (I. and II.) for the internal diazo-oxides. Successive nitration of the phenyl group gradually increases the stability of these p-diazoimines (Chem. Soc. Trans. 1908, 93, 604).

The para- diazoimides are produced from the acyl- and arylsulphonyl- derivatives of the para-diamines, and similar products are obtained from the arylsulphonyl-1 : 8-naphthylenediamines. The production of these diazoimides takes place in two stages, the diazonium salt first produced being decomposed by sodium acetate or mild alkali, yielding the internal condensation product ·

$$R\cdot SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot Cl \underset{HCl}{\overset{NaAc}{\rightleftharpoons}} R\cdot SO_2\cdot N\cdot C_6H_4N_2$$
V.   VI.
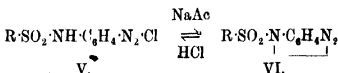
These para-diazoimides (VI.) are yellow sparingly soluble substances readily reconverted by strong acids into the corresponding diazonium salts. They combine additively with phenols, naphthols, naphthylamines, and their sulphonic acids, yielding azo- colouring matters (Morgan and Micklethwait, J. Soc Dyers and Colourists, 1909, 25, 107; cf. Chem. Soc. Trans. 1905, 87, 74, 921, 1302; 1906, 89, 1162; 1907, 91, 1509; 1908, 93, 615; Badische Anilin- und Soda-Fabrik D. R. P. 205037).

The foregoing general reaction has been extended further by the device of diazotising with liquid nitrogen trioxide in an anhydrous solvent such as acetone. In this way the simplest members of the series $Ac\cdot N:C_6H_4\cdot N_2$ have been obtained containing formyl, acetyl, and benzoyl groups (Morgan, Upton and Cleaze, Chem. Soc. Trans. 1917, 111, 187; 1918, 113.

III. DIAZOAMINES.

The diazoamines or diazoamino- compounds have the general formula $XN_2 \cdot NHY$, and may be either aromatic, mixed aromatic-aliphatic, or aliphatic in character, according as to whether X and Y are aromatic or aliphatic hydrocarbon radicals.

1. AROMATIC DIAZOAMINES.

The aromatic diazoamines are produced (1) by the action of nitrous acid (1 molecule) on two molecular proportions of a primary benzenoid amine ; (2) by coupling a diazonium salt with a primary or secondary benzenoid amine.

Diazoaminobenzene $C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5$, yellow crystals, m.p. 98°, is produced in quantitative yield by dissolving 10 parts of aniline in two parts of water containing 12 parts of hydrogen chloride, diazotising with 8 parts of sodium nitrite, and adding the diazo- solution to a solution of 10 parts of aniline in the calculated amount of hydrochloric acid. The diazoamine is precipitated on the addition of sodium acetate. (Absorption spectrum of diazoaminobenzene, Purvis, Chem. Soc. Trans. 1914, 105, 590.)

When warmed with aniline containing aniline hydrochloride, diazoaminobenzene is transformed into p-aminoazobenzene (v. AZO-COLOURING MATTERS), the velocity of transformation obeying the law of unimolecular reactions. When the transformation occurs below 40° a small proportion (about 4 p.c.) of o-amino-azobenzene is produced (F. H. Witt, Ber. 1912, 45, 2380 ; 1913, 46, 2557).

Diazoamino-p-toluene $C_7H_7 \cdot N_2 \cdot NH.C_7H_7$ is prepared in a similar manner, and undergoes transformation into an ortho-azo- compound, but the velocity of this change is only about one-ninth of that of the preceding transformation to para-azo- derivative.

The coupling of diazonium salts with meta-phenylenediamine, diphenylamine, the naphthylamines and their alkyl derivatives, leads directly to the production of azo- derivatives ; in these cases, intermediate diazoamines have not been isolated, except when the reactive ortho- or para- positions are already substituted (Morgan, Chem. Soc. Trans. 1902, 81, 91 ; 1907, 91, 370).

When an aromatic base, XNH_2^-, is coupled with a diazonium salt YN_2Cl, the resulting diazoamine is identical with that produced from XN_2Cl and YNH_2, and is generally regarded as being an equilibrium mixture of the two isomerides $XNH \cdot N_2Y$ and $XN_2 \cdot NHY$. This explanation assumes the migration of the diazo- group which has been observed to occur in several instances (Ber. 1882, 15, 2190 ; 1896, 29, 287 ; 1897, 30, 1412).

(For the constitution of the unsymmetrical aromatic diazoamines, $XNH \cdot N_2Y$, v. Meldola and Streatfeild, Chem. Soc. Trans. 1886, 49, 624 ; 1887, 57, 102, 434 ; 1886, 53, 664 ; 1889, 55, 412 ; 1890, 57, 785 ; cf. Forster and Garland $ibid.$ 1909, 95, 2051.)

2. ALIPHATIC-AROMATIC DIAZOAMINES.

The diazoamines containing one aliphatic and one aromatic group can be produced by (1) coupling a diazonium salt with an aliphatic amine (Ber. 1888, 21, 1016, 1112 ; 1889, 22, 938,

1302) ; (2) by treating an azide with Grignard reagent :

$$R \cdot N{\overset{\displaystyle N}{\underset{\displaystyle N}{\langle\;\|}}} + R' \cdot MgBr = R \cdot N(MgBr) \cdot N{:}NR'$$

$$H_2O \rightarrow R \cdot NH \cdot N{:}NR' + MgBr \cdot OH$$
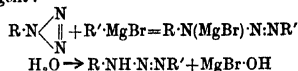
(Dimroth, Ber. 1903, 36, 909 ; 1905, 38, 670, 2328 ; 1907, 40, 2390). Diazoamines present the possibility of stereoisomerism, but their relative stability and the fact that they couple only slowly with β-naphthol, confirm the view that they are generally $anti$-diazo- compounds.

(For stereoisomeric diazoamines, v. J. Russ. Phys. Chem. Soc. 1906, 38, 578 ; Zeitsch. angew. Chem. 1900, 13, 762 ; 1902, 15, 1209.)

$Aromatic$ $bisdiazoamino$- $compounds$, e.g. $(C_6H_5 \cdot N_2)_2N \cdot C_6H_5$, have been obtained by the action of 2 molecular proportions of a diazonium salt on one of an aromatic amine (Ber. 1894, 27, 1863, 2597 ; 1895, 28, 170).

$Mixed$ $aliphatic$-$aromatic$ $bisdiazoamino$- $derivatives$ (v. Ber. 1888, 21, 1016 ; 1889, 22, 933 ; 1907, 40, 2390).

$Diazo$-ψ-$semicarbazines$ (v. Forster, Chem. Soc. Trans. 1906, 89, 223).

3. ALIPHATIC DIAZOAMINES.

Dimroth's general method may be applied to the production of purely aliphatic diazoamino- compounds. In this way, the simplest member of the series, **diazoaminomethane (dimethyltriazene)** $CH_3N{:}N \cdot NH \cdot CH_3$, has been prepared from methyl azide and magnesium methyl iodide. This substance, which is isolated by distilling its copper derivative with diazoaminobenzene under reduced pressure, is a colourless liquid, solidifying at $-12°$ and boiling at 92° (Dimroth, Ber. 1905, 38, 1575 ; 1906, 39, 3905).

IV. DIAZO- OXIDES.

When a diazonium salt couples with a phenol the product is generally an ortho or a para- hydroxyazo- compound (the C-azo- derivative), but in all probability, the O-azo- derivative is first produced, for in a few instances, when the velocity of transformation has been lessened by substitution, the intermediate O-azo- compound or diazo-oxide has been isolated. p-Bromo-benzenediazonium chloride and p-nitrophenol give p-$bromobenzenediazoate$-4 $oxynitrobenzene$

$$C_6H_4Br \cdot N{:}N \cdot O \cdot C_6H_4 \cdot NO_2$$
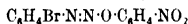
which, at 80°, becomes transformed into its isomeride, p-$bromobenzene$-2-azo-4-$nitrophenol$

$$C_6H_4BrN{:}N \cdot C_6H_4(NO_2)OH$$

(Ber. 1908, 41, 4027, 4304).

Occasionally traces of these intermediate diazoamines and diazo-oxides can be detected in the commercial azo- colouring matters (Vaubel, Zeitsch. Farben. Textil. Ind. 1902, 1, 3).

V. METALLIC DERIVATIVES OF DIAZO- COMPOUNDS.

In 1894 Schraube and Schmidt (Ber. 27, 514) found that on adding a 10 p.c. solution of p-nitrobenzenediazonium chloride to 18 p.c. aqueous sodium hydroxide at 50°–60°, a sodium diazo- derivative separated in yellow bronzy leaflets, to which they gave the formula

$$NO_2 \cdot C_6H_4 \cdot NNa \cdot NO_2H_2O$$
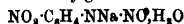
regarding the compound as the *sodium deriva-tive* of *p-nitrophenylnitrosamine*. This view of the constitution of the product was confirmed by the action on the compound of methyl iodide when *p*-nitrophenylmethylnitrosamine

$$NO_2·C_6H_4·N(CH_3)·NO$$
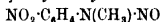
was obtained.

This sodium salt, which was regarded by Hantzsch as having the constitution of an anti-diazo- compound, **sodium *p*-nitrobenzenediazo-oxide** (*v. infra*), has been manufactured for use in the production of ' nitrosamino red ' (Badische Anilin- und Soda-Fabrik D. R. PP. 78874, 80263, 81134, 81202). The addition of excess of mineral acid to this metallic diazo- derivative, determines the regeneration of the original diazonium salt, but treatment with dilute acetic acid leads to the formation of a yellow product, *p-nitrophenylnitrosamine* $NO_2·C_6H_4·NH·NO$, a substance showing little tendency to couple with β-naphthol.

The silver derivative obtained from the foregoing sodium salt yields on methylation an oxygen ether $NO_2·C_6H_4·N:N·O·CH_3$, a re-action suggesting the possibility of tautomeric change. In many instances, two isomeric modifications of these metallic diazo- deri-vatives have been isolated.

Benzenediazonium chloride and cold concen-trated potassium hydroxide yield the normal *labile* form of *potassium benzenediazo-oxide* (I.), which readily couples with β-naphthol. The *stable* modification of *potassium benzenediazo-oxide* (II.) is produced by heating the strongly alkaline solution of the normal or labile salt at 130°-140°; this isomeride couples only very slowly with β-naphthol.

According to Hantzsch, these isomerides have respectively the following formulæ :—

$$\begin{array}{cc} C_6H_5·N & C_6H_5·N \\ \| & \| \\ KO·N & N·OK \end{array}$$

I. *Syn*- (labile form).　II. *Anti*- (stable form).
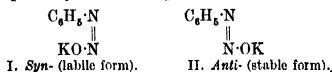
Dobbie and Tinkler (Chem. Soc. Trans. 1905, 87, 273) have found, however, that these iso-meric potassium salts have totally different ultra-violet absorption spectra. But as stereo-isomerides, like the benzaldoximes, have iden-tical absorption spectra, it seems probable that the above isomeric salts are structurally dis-similar. Confirmation of the stereochemical theory would be obtained by isolating the *anti-*diazohydroxide from the stable (*anti-*) potassium salt, but on treating this with an acid, the nitro-samine separates. Moreover, the product sup-posed by Hantzsch and Pohl to be an *anti-*diazohydroxide (Ber. 1902, 35, 2964) was shown by Orton to be a mixture of quinonediazide and a hydroxyazo- compound (Proc. Roy. Soc. 1903, 71, 153 ; Chem. Soc. Trans. 1903, 83, 796).

The existence of the *syn-* diazohydroxides is doubtful, and diazonium hydroxides (*v. supra*) are only known in solution.

Diazo-anhydrides $R·N:N·O·N:NR$ or $R·N·O·N:NR$ are very unstable explosive com-
Ṅ
pounds produced by the action of acetic acid on the metallic *syn-* diazo-oxides. The *anti-* diazo-oxides, when thus treated, give nitro-samines.

Aromatic diazoic acids $Ar·N_2O_2H$. Benzene-

diazoic acid, produced by oxidising potassium diazoic acid, produced by oxidising potassium benzenesyndiazo-oxide or -isodiazo-oxide with potassium ferricyanide in alkaline solution, is obtained in sparingly soluble white leaflets (m.p. 46°) dissolving readily in organic solvents or alkalis. With mineral acids it is transformed into *o*- and *p*-nitroaniline, and with hypo-chlorites it yields 4-chloro-2-nitroaniline. Its sodium salt gives the α- or *N*-ester $C_6H_5·N(CH_3)·NO_2$, the silver salt furnishes the β- or *O*-ester, $C_6H_5·N:NOO·CH_3$. Since the acid is also obtained by the action of nitrogen pentoxide on aniline it is probably a tautomeric substance $C_6H_5·NH·NO_2 \rightleftharpoons C_6H_5·N:NO_2H$ (Bam-berger, Ber. 1893, 26, 471; 1894, 27, 359, 914, 584, 1273; Hantzsch, Ber. 1902, 35, 258).

VI. DIAZO- CYANIDES.

The addition of the calculated amount of potassium cyanide to a cold acid solution of a diazonium salt determines the formation of a sparingly soluble diazo- cyanide. In many instances, two modifications of the diazo-cyanides can be distinguished, and these varieties are regarded by Hantzsch as being stereoiso-meric forms. *p*-Chlorobenzenediazonium chlor-ide, from *p*-chloraniline, yields first the yellow labile *syn-p*-**chlorobenzenediazocyanide** (I.), which readily evolves nitrogen, yields

$$\begin{array}{cc} C_6H_4Cl·N & C_6H_4Cl·N \\ \| & \| \\ CN·N & N.CN \end{array}$$
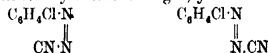
I. *Syn*-diazocyanide.　II. *Anti*-diazocyanide.

p-chlorobenzonitrile on treatment with copper powder, and passes into the stable *anti-p*-**chloro-benzenediazocyanide** (II.). The latter sub-stance, which is not affected by copper powder, may be distilled in steam without decomposition.

Confirmation of this stereochemical theory of the constitution of the diazo-cyanides has been obtained by a study of the cyanides de-rived from *p*-methoxybenzenediazonium chlor-ide. This salt with potassium cyanide in alcoholic solution yields the *syn-*diazocyanide (III.), an orange-red insoluble substance (m.p. 51°), which couples with β-naphthol and slowly changes into the non-coupling *anti - diazo-*cyanide (IV.), a brownish - red compound, melting at 121°.

$$\begin{array}{cc} CH_3·O·C_6H_4·N & CH_3·O·C_6H_4·N \\ \| & \| \\ CN·N & N·CN \end{array}$$

III.　　IV.
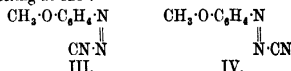
The existence of a third isomeric cyanide is indicated by evaporating at the ordinary tem-perature in the presence of excess of hydro-cyanic acid, an aqueous solution of *p*-methoxy-benzenediazonium hydroxide. The colourless crystalline product has the composition :

$$CH_3O·C_6H_4·N_2·CN, HCN, 2H_2O$$
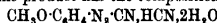
and possesses all the properties of a true metallic salt ; it is very soluble, and its solution is an electrolyte. Moreover, this double salt couples with β-naphthol, and is converted by alkalis into the yellow *syn-*diazo cyanide. These properties correspond with those of the normal diazonium salts, and the foregoing soluble cyanide is re-garded as having the following constitution :

$$CH_3·O·C_6H_4·N·CN$$
$$Ṅ$$
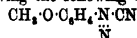
(Hantzsch, Ber. 1900, 33, 2161 ; 1904, 34, 4166).

The two pairs of diazo- cyanides from *p*-chloraniline and *p*-anisidine were examined spectroscopically by Dobbie and Tinkler, who found that each pair gave almost identical ultra-violet absorption spectra, whereas the above soluble diazonium cyanide gave an entirely different spectrum. These results are in accordance with Hantzsch's view of the configuration of the diazo- and diazonium cyanides (Chem. Soc. Trans. 1905, 87, 273).

It has, however, been suggested by several workers in this field that the isomerism of the diazo- cyanides is structural, the *syn*- compounds being *iso*-cyanides R·N:N·NC and their *anti*-isomerides, cyanides R·N:N·CN (Ber. 1895, 28 861 ; Chem. Soc. Trans. 1903, 83, 805).

VII. DIAZO- SULPHONATES.

Although the stereochemical theory of the constitution of diazo- cyanides is supported by physical as well as chemical evidence, yet it is significant that the only other series of salts in which this isomerism has been detected is one derived from sulphurous acid, a substance resembling hydrocyanic acid in giving rise to organic isomeric derivatives which are structurally dissimilar.

The diazo- sulphonates, prepared by adding potassium sulphite to aqueous solutions of benzenoid diazonium chlorides, frequently exist in two differently coloured modifications, but in most cases the *syn*- isomeride is too unstable to be isolated in a pure state.

Potassium syn-2.4-diiodobenzenediazosulphonate (I.) is an orange substance, whilst the *anti*-salt (II.) is yellow :

$$C_6H_3I_2\cdot N \qquad\qquad C_6H_3I_2\cdot N$$
$$\parallel \qquad\qquad\qquad\qquad \parallel$$
$$KSO_3\cdot N \qquad\qquad\quad N\cdot SO_3K$$
$$I. \qquad\qquad\qquad\qquad II.$$
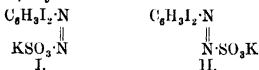
The diazotised naphthylamines behave exceptionally, yielding only *syn*-diazosulphonates, which, on warming pass, not into their *anti*-isomerides, but into the corresponding azo-naphthalenes (Ber. 1897, 30, 71).

The *syn*- and *anti*- modifications of **potassium benzenediazosulphonate** $C_6H_5\cdot N$:$N\cdot SO_3K$, were found by Dobbie and Tinkler (*l.c.*) to have identical ultra-violet absorption spectra. This fact supports the stereochemical theory of their structures (*cf.* Ber. 1894, 27, 1726, 2099, 2586, 2930, 3527 ; 1895, 28, 242, 447, 834, 861 ; J. pr. Chem. 1894, [ii.] 50, 239 ; Meyer and Jacobsen, Lehrbuch der Org. Chem. ii. 303).

VIII. ALIPHATIC DIAZO- COMPOUNDS.

The amines of the aliphatic series, when treated with nitrous acid, generally lose their basic nitrogen, the amino- group becoming replaced by hydroxyl. In some cases, however, the nitrogen is retained and an aliphatic diazo-compound is produced, having the general

$$\text{formula } RH\cdot C\begin{array}{c} N \\ \parallel \\ N \end{array}\text{ with the azo- group attached}$$

entirely to the same carbon atom.

An alternative formulation has been suggested for the aliphatic diazo- compounds in which one nitrogen is quinquevalent, so that

the general formula becomes :$>$C:N$\vdots$N (Thiele, Ber. 1911, 44, 2522; Forster and Cardwell, Chem. Soc. Trans. 1913, 103, 861; *cf.* Ber. 1912, 45, 1654; 1916, 49, 1884.

Although glycine is converted by nitrous acid or alkyl nitrites into glycollic acid, yet its ethyl ester gives rise to **ethyl diazoacetate** N_2:$CH\cdot CO_2\cdot C_2H_5$, a yellow liquid freezing at 24° and boiling at 143°-144°/72 mm. (Curtius, Ber. 1883, 16, 2230).

One kilogram of ethyl aminoacetate hydrochloride and 750 grams of sodium nitrite are added successively to 2 litres of water containing 5 grams of sodium acetate. The mixture is shaken until the temperature falls to 0°; 5 c.c. of 10 p.c. sulphuric acid and 500 c.c. of ether are added and the liquids thoroughly agitated. The ethereal layer is separated and the treatment with dilute acid and ether repeated until red fumes are evolved. The ethereal extracts are washed with dilute aqueous sodium carbonate till alkaline, dried with calcium chloride, and the solvent removed on the water-bath. The yield of ethyl diazoacetate is 94·7 p.c. of the calculated quantity (Silberrad, Chem. Soc. Trans. 1902, 81, 600).

With iodine, ethyl diazoacetate yields diiodoacetic acid, and with aldehydes it condenses to form ketonic esters :

$$R\cdot CHO + N_2\text{:}CH\cdot CO_2\cdot C_2H_5$$
$$\to R\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5$$
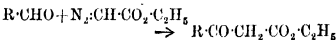
One of the most remarkable reactions of this diazo- ester is its condensation with benzene and its homologues, giving rise to a series of esters containing seven-membered hydrocarbon rings (Bucherer, Ber. 1896-1903, 29, 106 ; 30, 632, 1949 ; 31, 399, 402, 2004, 2241, 2247 ; 32, 705 ; 33, 184 ; 36, 3509 ; Annalen, 1908, 358, 1).

Ethyl diazoacetate, when heated with alkalis undergoes a series of complex polymeric changes (Curtius, Ber. 1885, 18, 1283 ; 1906, 39, 1383, 3398, 4140 ; 1907, 40, 84, 815, 1176, 1194, 1470 ; 1908, 41, 3116, 3140, 3161 ; J. pr. Chem. 1888, [2] 38, 408 ; Hantzsch, Ber. 1900, 33, 58 ; *cf.* Chem. Soc. Trans. 1902, 81, 598).

Diazo- derivatives are not obtained from free α-amino-carboxylic acids, and only from those amino-esters of aliphatic acids containing the amino- group in the α-position with respect to alkylated carboxyl group. The esters of those polypeptides which contain the amino-group in the α-position to a carboxyl- group can also be transformed into diazo- derivatives.

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$$
$$\to N_2\text{:}CH\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$$
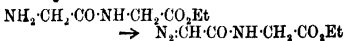
The α-aminoketones (*e.g.* α-aminoacetophenone $C_6H_5\cdot CO\cdot CH_2\cdot NH_2$) give diazo- compounds (Ber. 1904, 37, 2080), and so also do certain uric acid compounds, *e.g.* aminomethyluracil.

Diazomethane $CH_2\begin{array}{c} N \\ \diagdown \parallel \\ N \end{array}$, or CH_2:N:N, the

simplest aliphatic diazo- compound, is prepared by adding methyl-alcoholic potassium hydroxide to an ethereal solution of nitrosomethylurethane

$$C_2H_5\cdot O\cdot CO\cdot N(CH_3)\cdot NO$$
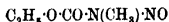
and distilling the mixture on the water-bath, when the distillate consists of an ethereal solution of the diazo- compound, the yield being

50 p.c. of the calculated quantity. This substance is also produced by the action of hydroxylamine on dichloromethylamine

$$CH_3 \cdot NCl_2 + H_2NOH = CH_2:N_2 + H_2O + 2HCl$$
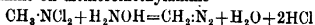
Diazomethane is a poisonous yellow gas condensing in snow and calcium chloride to a yellow liquid boiling below $0°$. It is a powerful methylating agent, converting hydroxyl groups into methoxyl, and alkylating primary and secondary bases.• With iodine, diazomethane gives nitrogen and methylene iodide, and aldehydes are converted into methyl ketones (*cf.* Monatsh. 1905, 26, 1295, 1311; Ber. 1907, 40, 479; 1908, 41, 3199; 1909, 42, 2559; Chem. Soc. Trans. 1908, 93, 242).

Diazomethane combines additively with unsaturated compounds; with acetylene it gives pyrazole (Ber. 1898, 31, 2910), and with ethyl fumarate it furnishes ethyl pyrazolinecarboxylate.

Diazoethane $CH_3 \cdot CH : N_2$ and **phenyldiazomethane** $C_6H_5 \cdot CH:N_2$ have both been prepared (Ber. 1902, 35, 897). The former closely resembles diazomethane, the latter is a dark-red oil.

Substitution increases considerably the colour of these diazo- derivatives; dimethyldiazomethane $C(CH_3)_2:N_2$ is red and diphenyldiazomethane is obtained in bluish red needles melting at $20°$ (Staudinger, Ber. 1916, 49, 1884).

Diazomethane should not be confused with **azomethane** $CH_3 \cdot N:N \cdot CH_3$, the simplest azo-compound which is produced by oxidising symmetrical dimethylhydrazine (hydrazomethane) with chromic acid (Thiele, Ber. 1909, 42, 2575). Azomethane is a colourless gas condensing to a pale yellow liquid (b.p. $1·5°$).

Diazomethanedisulphonic acid, a noteworthy example of an aliphatic diazo-compound, results from the interaction of potassium cyanide and potassium bisulphite in presence of caustic potash. The solution, acidified and treated with nitrous acid, yields successively ammomethanedisulphonic acid and the diazo- compound. Sulphurous acid and diazomethanedisulphonic acid yield an additive compound which, on boiling, furnishes hydrazine (V. Pechmann, Ber. 1895, 28, 2374; 1896, 29, 2161).

Diazoacetone $CH_3 \cdot COCH:N_2$, a pale yellow liquid, is obtained from aminoacetylacetone by converting this base into diazoacetylacetone anhydride and treating this product with aqueous caustic alkali (Wolff, Annalen, 1912, 394, 23).

Metallic diazo- derivatives of the aliphatic series are produced by treating nitrosoalkyl urethanes with concentrated caustic potash solution or ethereal potassium ethoxide. **Potassium methyldiazo-oxide** $CH_3 \cdot N:B \cdot OK, H_2O$ separates in white crystals, when nitrosomethylurethane is added to concentrated aqueous caustic potash at $0°$. **Potassium benzyldiazo-oxide**

$$C_6H_5 \cdot CH_2 \cdot N:N \cdot OK, H_2O$$
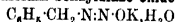
is similarly prepared from nitrosobenzylurethane. These metallic derivatives are very unstable; they are decomposed by water with explosive violence, yielding respectively diazomethane and phenyldiazomethane (Hantzsch and Lehmann, Ber. 1902, 35, 897).

Bibliography.—Hantzsch, Die Diazoverbindungen, Ahren's *Sammlung*, 1902; Morgan, Our Present Knowledge of Aromatic Diazo-' Compounds, Brit. Assoc. Report, 1902; Eibner, Zur Geschichte der Aromatischen Diazoverbindungen, 1903; Cain, The Chemistry and Technology of the Diazo- Compounds, 1920.

G. T. M.

DIAZOACETATE ETHYL *v.* DIAZO- COMPOUNDS.

DIAZOAMINOMETHANE *v.* DIAZO- COMPOUNDS.

DIAZOANTHRANILIC ACID *v.* DIAZO-COMPOUNDS.

DIAZOBENZENE, *Benzenediazonium* (*v.* DIAZO- COMPOUNDS)

DIAZOBENZENE SULPHONIC ACID *v.* DIAZO- COMPOUNDS.

DIAZOIMIDES, DIAZOIMINES *v.* DIAZO-COMPOUNDS.

DIAZOMETHANE *v.* DIAZO- COMPOUNDS.

DIAZURINE *v.* AZO- COLOURING MATTERS.

DIBASIC ACIDS. *Oxalic acid series.* A numerous and important group of acids, having the general formula $C_nH_{2n-2}O_4$. The lowest member of the series is *oxalic acid* $C_2H_2O_4$, and the highest member at present known, *dicetyladipic acid* $C_{36}H_{74}O_4$. As the radical C_nH_{2n} is capable of existing in a variety of ways, it follows that these acids may exist in many isomeric forms. Unlike the fatty acids, the lowest members of the oxalic acid series are solids.

The naturally occurring acids exist partly free and partly as salts or esters. Thus oxalic acid occurs chiefly as the potassium salt in different varieties of *Oxalis* and *Rumex*; malonic acid, as the calcium salt, is found in the sugar beet; succinic acid in amber, certain varieties of lignite, resins, turpentine oils, and animal fluids; rocellic acid in *Rocella tinctoria* (D. C.). Other members of this series are obtained by the oxidation of naturally occurring substances. Thus suberic acid is obtained by boiling cork with nitric acid; azelaic acid by the oxidation of castor oil; adipic acid by the oxidation of suet or tallow, whilst homologues of succinic, glutaric and adipic acids are frequently obtained in the oxidation of derivatives of the terpene compounds. The higher members of the series are prepared by the oxidation of members of the fatty acid series.

General methods of preparation.

(1) By the oxidation of the diprimary glycols, primary hydroxyaldehydes, dialdehydes, primary hydroxy- acids, or aldehyde-acids; *e.g.* glycol, glycollic acid, glyoxal, or glyoxylic acid → oxalic acid.

(2) By the oxidation of the fatty acids or of acids of the oleic acid series; *e.g.* erucic acid → brassylic acid.

(3) By the reduction of unsaturated dicarboxylic acids; *e.g.* fumaric acid → succinic acid.

(4) By the action of silver (powder) on mono-iodo- (or bromo)- fatty acids; *e.g.* β-iodopropionic acid → adipic acid.

Exception.—The reaction is abnormal when α-bromisobutyric acid is used, di- and tri- alkylglutaric acids being produced. •

(5) By the conversion of monohalogen- substituted fatty acids or of the halogen addition products of the alkylenes C_nH_{2n} into cyanderivatives and saponification of the latter;

e.g. cyanacetic acid → malonic acid; ethylene dicyanide → adipic acid.

(6) By the replacement of the hydrogen atoms of the CH₂ group in the malonic esters by various alkyl- groups; *e.g.* sodium malonic ester and methyl iodide → *iso*-succinic ester.

(7) By the electrolysis of concentrated solutions of potassium alkyl salts of the dicarboxylic acids; *e.g.* potassium ethyl malonate →diethyl succinate.

(8) By the introduction of acid residues into the acetoacetic esters, and decomposition of the product with alkali; *e.g.* acetosuccinic ester → succinic acid.

(9) By the decomposition of tricarboxylic acids containing two carboxyl- groups attached to the same carbon atom; *e.g.* ethanetricarboxylic acid → succinic acid.

The acids of this series behave differently on the application of heat, depending upon the position of the carboxyl groups. Oxalic acid, the first member of the series, breaks down on heating mostly into carbon dioxide, carbon monoxide, and water, and partly into carbon dioxide and formic acid. This latter decomposition is typical of those homologues of oxalic acid in which the two carboxyl- groups are attached to the same carbon atom; they are the β-dicarboxylic acids, and of these malonic acid is the type. On application of heat, malonic acid splits into acetic acid and carbon dioxide. The next class, the γ-dicarboxylic acids, in which the two carboxyl- groups are attached to adjacent carbon atoms, when heated, lose a molecule of water and pass into anhydrides. Succinic acid is the type of these acids. Acids, such as glutaric acid, in which the carboxyl- groups are attached to two carbon atoms separated by a third, behave similarly to the γ-dicarboxylic acids, but form anhydrides less readily. When the carbon atoms to which the carboxyl- groups are attached are separated by two carbon atoms, *e.q.* adipic acid, they do not influence one another on the application of heat. For these reasons, the paraffin dicarboxylic acids are arranged in different groups, the general properties of which will be discussed under MALONIC ACID, SUCCINIC ACID, and GLUTARIC ACID, which are types of the several groups mentioned above.

(For melting-points of the dibasic acids, *v.* Massol, Bull. Soc. chim. [3] 21, 578; melting-points of their esters, *v.* Schneider, Zeitsch. physikal. Chem. 22, 228;· electrical conductivity of the acids, *v.* Walden, *ibid.* 8, 448; volatility in steam, *v.* Auwers, Annalen, 292, 159.)

DIBENZIL *v.* KETONES.

DI-*iso*-BUTYLACETIC ACID *v.* DECATOIC ACIDS.

2·6·DI-*iso*-BUTYLPIMELIC ACID

$$CH_2[CH_2·CH(C_4H_9)·CO_2H]_2$$
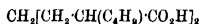
Prepared by heating 1·5·di-*iso*-butylpentane-tetracarboxylic acid at 200°-220° (Perkin and Prentice, Chem. Soc. Trans. 1891, 842); m.p. 82°-84°.

DICENTRINE $C_{20}H_{21}O_4N$ occurs with protopine in *Dicentra pusilla* (Sieb. and Zucc.) and possibly in *D. formosa* (Walp.). Prismatic crystals, m.p. 168°-169°, $[a]_D +62°$ in chloroform. Salts crystalline (Heyl. Arch. Pharm. 1903, 241

313; Asahina, *ibid.* 1909, 247, 201). Produces slight narcosis (Iwakawa, Arch. expt. Path. Pharm. 1911, 64, 369). Gadamer has stated (Arch. Pharm. 1911, 249, 680) that dicentrine resembles glaucine in its properties, and suggests that it is glaucine in which the two —OMe groups in positions 5 and 6 are replaced by a dioxymethylene group.

DICETYLADIPIC ACID $C_{38}H_{74}O_4$. Prepared by heating dicetylbutanetetracarboxylic acid to 205° (Lean, Chem.`Soc. Trans. 1894, 1016). Two isomerides are thus produced, which may be separated by crystallisation from alcohol, α-acid, m.p. 42°-43°; β-acid, m.p. 32°-34°.

DICETYLIC ACID $CH(C_{16}H_{32})_2COOH$ is obtained by heating dicetylmalonic acid; m.p. 69°-70° (Guthzeit, Annalen, 206, 365)

DICETYLMALONIC ACID

$$(C_{16}H_{33})_2C(CO_2H)_2$$
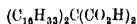
The ethyl ester is formed by treating diethylmalonic ester with sodium methoxide and cetyl iodide; the ester is decomposed with a concentrated solution of caustic potash; m.p. 86°-87° (Guthzeit, Annalen, 206, 362).

DICHLORAMINET. Toluene-*p*-sulphone dichloramine.

2 : 5-DICHLOROANILINE

Prepared by reducing 2 : 5-dichloronitrobenzene with iron and hydrochloric acid; m.p. 50°; b.p. 246°/744 mm. Used in making the chloramine dyes.

2 : 5 - DICHLOROANILINE - 4 - SULPHONIC ACID

2 : 5-dichloroaniline. Soluble in hot water. Sodium salt with 5 molecules H_2O readily soluble (Noelting and Kopp, Ber. 1905, 38, 3513).

1 : 5-DICHLOROANTHRAQUINONE

is obtained by boiling an aqueous solution of alkali anthraquinone-1 : 5-disulphonate with hydrochloric acid and sodium chlorate (Ullmann and Knecht, Ber. 1911, 44, 3125; Farbenfab. vorm. F. Bayer & Co., D. R. P. 205195). Also by suspending 1 : 5-diaminoanthraquinone in hydrochloric acid, diazotising at 5°-10°, and treating the solution with cuprous chloride dissolved in hydrochloric acid (*idem.* D. R. P. 131538). Citron-yellow needles, readily soluble in hot toluene, sparingly soluble in alcohol; m.p. 251°. Used in making indanthrene violet (*q.v.* art. INDANTHRENE).

3 : 3′-DICHLOROBENZIDINE
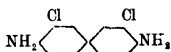
Prepared by chlorinating a sulphuric acid solution of diacetyl benzidine (made by boiling benzidine with glacial acetic acid) with bleaching

powder or sodium hypochlorite solution, filtering, adding hydrochloric acid, and hydrolysing the product (Levinstein, Eng. Pat. 25725, 1896). May also be obtained by reducing o-chloronitrobenzene in an alkaline solution by means of zinc dust (cf. Cohn, Ber. 1900, 33, 3551).

DICHLOROCARBAMIDE v. HYDRAZINES.

DICHLOROPHTHALIC ACIDS v. PHTHALIC ACID.

2′ : 5′-DICHLORO-4′-SULPHO-1-PHENYL-3-METHYL-5-PYRAZOLONE. Prepared by condensing ethyl acetoacetate with 2 : 5-dichlorophenylhydrazine-4-sulphonic acid (D. R. P. 222405). Used in making Xylene yellow (see PYRAZOLONE COLOURING MATTERS).

DICHROITE v. IOLITE.

DICYANDIAMIDE, Cyanoguanidine

$$NH_2(NH:)C\cdot NH\cdot C:N$$
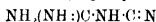
Obtained by the polymerisation of cyanamide in aqueous solution on long standing or on warming, especially after addition of a drop of ammonia (Beilstein and Geuther, Annalen, 108, 99 ; 123, 241 ; Haag, ibid. 122, 22) ; by treating thiourea with mercuric amline (Montecchi, Gazz. chim. ital. 28, ii. 434) Prepared by heating ammonium sulphate and sodium cyanamide on the water-bath ; cyanamide separates as a yellow oil, which, after some hours, with frequent shaking, changes into dicyandiamide (Hermann, Monatsh. 1905, 1025). Soll and Stutzer (Ber. 1908, 4534) make crude calcium nitride into a paste with water and heat to boiling. The hot liquid is filtered by suction, and dicyandiamide separates out from the filtrate. Crystallises in needles ; m.p. 205° (Pohl, J. pr Chem. 77, [2] 533). By warming with dilute acids, it is transformed into dicyandiamidine (guanyl urea) $NH_2(NH:)C\cdot NH\cdot CO\cdot NH_2$. It is used in quantitative analysis to separate nickel from cobalt. The solution containing nickel and cobalt is made alkaline, and to it is added a small quantity of sugar solution. To this is added dicyandiamidine sulphate (prepared by dissolving dicyandiamide in dilute sulphuric acid), whereby the nickel salt of dicyandiamidine is precipitated, the cobalt remaining in solution. The precipitate is filtered through a Gooch crucible, dried at 115°–160°, and weighed as anhydrous nickel dicyandiamidine $Ni(C_2H_3N_4O)_2$ (Grossmann and Schück, Analyst, 1910, 247 ; 1909, 455 ; 1907, 273, 394). Dicyandiamide is reduced by zinc and dilute hydrochloric acid at the ordinary temperatures to methylamine and guanidine, the methylamine being formed by the reduction of the prussic acid first produced (Bamberger and Seeberger, Ber. 1893, 1583) ; a mixture of nitric and sulphuric acids converts it into nitrodicyanodiamidine (Thiele and Uhlfelder, Annalen, 303, 107) ; it condenses with dialkylcyanacetic or malonic esters yielding pyrimidine derivatives ; thus with diethylcyanacetic ester a condensation product is obtained which yields diethylbarbituric acid on treatment with sulphuric acid (Bayer & Co., D. R. P. 165223 ; Chem. Zentr. 1906, i. 514). All manures containing calcium cyanamide contain also dicyandiamide, formed by the spontaneous polymerisation of the calcium cyanamide ; it is not poisonous to plants if not used in too large quantities (Perotti, Atti. R. Accad. Lincei, 15, i. 48 ; Chem. Zentr. 1909, i. 1497 ; Inouye, J. Soc.

Chem. Ind. 1909, 1054 ; Aso, ibid.). The Cyanide-Gesellschaft (Chem. Zentr. 1904, ii. 1079 ; D.R.P. 154505) treat calcium carbide or a carbide-forming mixture with nitrogen, lixiviate the mass with water, and use the product, which contains calcium cyanamide, dicyandiamide, &c., as a manure (v. also Frank, Zeitsch. angew. Chem. 19, 835). The constitution of dicyandiamide is regarded as $NH_2(NH:)C\cdot NH\cdot C:N$ or the tautomeride $(NH_2)_2C:N\cdot C:N$ (Bamberger, Ber. 1883, 1459 ; 1891, 899 ; Biltz, J. pr. Chem. 77, [ii.] 533 ; Pranichnikov, J. Soc. Chem. Ind. 1909, 724).

DIDYMIN v. SYNTHETIC DRUGS.

DIDYMIUM v. PRASEODYMIUM and NEODYMIUM.

DIETHYLACETIC ACID. Pseudo-caproic acid (v. CAPROIC ACID).

DIETHYLALLOXAN v. ALLOXAN.

DIETHYLAMINE v. under Ethylamines, art. ETHYL.

p-DIETHYLAMINOBENZOIC ACID

$$CO_2H\langle\ \rangle N(C_2H_5)_2$$
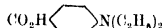
Prepared by the action of carbonyl chloride on diethylaniline or by ethylating p-aminobenzoic acid ; m.p. 188°.

DIETHYL-m-AMINOPHENOL

$$\overset{OH}{\underset{}{\langle\ \rangle}} N(C_2H_5)_2$$
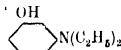
Formed by heating m-aminophenol hydrochloride with ethyl alcohol under pressure (Bad. Anil. und Soda Fabrik, D. R. P. 44002) ; by heating resorcinol with diethylamine (Leonhardt & Co., D. R. P. 49060) ; by alkali fusion of diethylaniline-m-sulphonic acid (Soc. Chem. Ind. Basle, D. R. P. 44792). For details of the last-named process as used on the large scale, see Cain, Intermediate Products for Dyes ; m.p. 78° ; b.p. 201°/25 mm. Used in the manufacture of rhodamine B.

DIETHYLANILINE $\langle\ \rangle N(C_2H_5)_2$. Obtained by heating aniline hydrochloride with ethyl alcohol under pressure ; or, better, by heating aniline hydrobromide with ethyl alcohol at 145°–150° (Stadel, D. R. P. 21241), or by treating aniline with ethyl alcohol in presence of iodine at 235° (Knoll & Co., D. R. P. 250236) ; m.p. −38·1° ; b.p. 216·5° ; sp.gr. 0·930 at 18°.

DIETHYLANILINE-m-SULPHONIC ACID

$$\overset{SO_3H}{\underset{}{\langle\ \rangle}} N(C_2H_5)_2$$
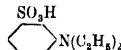
Is prepared by acting on diethylaniline with fuming sulphuric acid.

DIETHYLDIACETOSUCCINATE v. KETONES.

DIETHYL OXALACETATE v. KETONES.

DIETHYLSAFRANIN v. AZINES.

DIETZEITE. A double iodate and chromate of calcium crystallising in the monoclinic system, discovered in 1891 in the sodium nitrate deposits of Atacama, Chile. Analyses lead to the formula $7Ca(IO_3)_2\cdot 8CaCrO_4$, but the simple double salt formula $Ca(IO_3)_2\cdot CaCrO_4$ appears more probable. Distinct crystals are rare, the mineral usually forming crystalline fibrous aggregates of a dark gold-yellow colour. Sp.gr.

3·698. It is soluble in hot water; on cooling crystals of hydrated calcium iodate $(Ca(IO_3)_2 + 6H_2O)$ separate, leaving the calcium chromate in solution. The simple calcium iodate $(Ca(IO_3)_2)$ called lautarite occurs in the same deposits.

L. J. S.

DIFFUSION. In any gaseous mixture or liquid solution, even when protected from mechanical disturbances and kept at a uniform temperature throughout, the composition ultimately becomes the same at all points, whatever the original distribution of the gaseous or dissolved substances may have been. The process by which this condition is reached is termed 'diffusion,' and it depends, not on the circulation of the unequally distributed substances as a whole, but on molecular movement. According to the kinetic theory, a mass of gas which, as a whole, is at rest, is yet the scene of great activity on the part of the constituent molecules. These are endowed with a high velocity, and alter the direction of their motion only when they collide with one another or with the walls of the containing vessel. If this point of view is adopted, then the occurrence of diffusion in a mixture of irregularly distributed gases becomes intelligible. There are, moreover, many experimental grounds for extending the kinetic theory to the liquid state, and for the view that the molecules of a liquid also are in a state of constant motion. With this conception the phenomenon of diffusion of a dissolved substance is obviously in harmony.

Diffusion of Gases.

When two vessels containing different gases at the same temperature and pressure are put into free communication, each gas penetrates the other until its partial pressure is uniform in both vessels. The experimental investigation of this phenomenon on quantitative lines is not easy, but it appears to be well established that the diffusion coefficient of each gas varies from point to point of the diffusion system (*see* Loschmidt, Sitzungsber. Akad. Wiss. Wien, 1870, 61, 367; 1870, 62, 468; von Obermayer, *ibid.* 1880, 81, 1102; 1882, 85, 147, 748; 1883, 87, 188; 1887, 96, 546; Waitz, Ann. Physik, 1882, 17, 201, 351; ·Lonius, *ibid,* 1909, 29, 664).

When the concentration of a gas is maintained constant at one point of a gas system and zero at another point, a static condition of affairs is established analogous to what is observed when one end of a metal bar is kept at a high temperature and the other end at a low temperature. If, for instance, a tall cylinder, communicating freely with the atmosphere, contains at the bottom a layer of caustic alkali, there is a regular concentration gradient from the top downwards, tlfe carbon dioxide being completely absorbed at the surface of the alkali. Provided the concentration difference between the top and bottom of the cylinder is maintained constant, a steady condition of diffusion is attained, and the rate of flow of the carbon dioxide, as deduced from the amount absorbed by the alkali, is inversely proportional to the length of the diffusion column (*see* Brown and Escombe, Phil. Trans. B, 1900, 193, 223; *also* Winkelmann, Ann. Physik, 1884, 22, 1, 152).

Much attention has been devoted to the phenomenon of diffusion across porous diaphragms, through capillary tubes, and from narrow apertures. Graham showed (*see* Chemical and Physical Researches, p. 44) that the exchange of two gases across a porous diaphragm, the pressure on the two sides remaining the same, takes place in such a way that the volumes of the gases diffused in a given time are inversely proportional to the square roots of their densities. This observation is of very great interest in connection with the kinetic theory, from the assumptions of which it follows that the mean velocity of the molecules of a gas is inversely proportional to the square root of its density. Graham's law is not accurate except when the diaphragm is extremely thin, but it is nevertheless the basis of a method for separating two gases of different densities. Thus, for instance, when a mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume is passed at a suitable rate through a train of clay-pipe stems, the gas collected at the further end will ignite a glowing splint. By experiments of this kind it was shown that atmospheric nitrogen is a mixture of at least two gases of different density (*see* Rayleigh and Ramsay, Phil. Trans. 1895, 186, 206). The operation of separating gases by this method is termed 'atmolysis.'

In the passage of a gas through a capillary tube—'transpiration,' as it is sometimes called—friction generally plays a considerable part, but it has been found that if the diameter of the tube is small in comparison with its length and with the mean free path of the gas molecules, then the quantity of gas passing through a given tube in unit time is inversely proportional to the square root of the density (Knudsen, Ann. Physik, 1909, 28, 75).

The time required for the escape or 'effusion' of a given volume of gas through a fine aperture in a thin plate into a vacuum is approximately proportional to the square root of the density of the gas. The thinner the plate and the smaller the aperture, the more nearly is this relationship fulfilled (*see* Graham, Chemical and Physical Researches, p. 88; Bunsen, Gasometry, p. 121; Timoféeff, Zeitsch. physikal. Chem. 1890, 6, 586; Donnan, Phil. Mag. 1900, 49, 423; Emich, Monatsh. 1903, 24, 747; Knudsen, Ann. Physik, 1909, 28, 999). An apparatus for determining the relative density of two gases, based on this principle, has been described by Bunsen (*l.c.*) (*v.* SPECIFIC GRAVITY).

The passage of a gas across a diaphragm takes place, not only when the diaphragm is porous In the ordinary sense, but also when it has the power of dissolving or absorbing the gas. Thus, at high temperatures, platinum and palladium absorb considerable quantities of hydrogen, and this gas readily diffuses through the walls of a vessel made of either metal. Winkelmann (Ann. Physik, 1901, 6, 104; 1902, 8, 388 1905, 16, 773; 17, 589; Richardson, Nicol & Parnell, Phil. Mag., 1901, 8, 1; Schmidt, Ann. Physik, 1904, 13, 747) has shown that the rate of diffusion of hydrogen through glowing platinum or palladium is not, as might be expected, proportional to the pressure of the hydrogen; at lower pressures the gas diffuses relatively more rapidly. The experimental data seem to indicate that it is the atoms, not the molecules, of hydrogen which can pass through the metal.

On the ability of hydrogen and the inability of other gases to diffuse through heated palladium, there is based the osmotic cell described by Ramsay (Phil. Mag. 1894, 38, 206).

The rate of diffusion of gases across a layer of water or aqueous solution depends mainly on the solubility and the density of the gas. According to Exner, who made experiments on the diffusion of gases across a film of soap solution, the velocity is, *cæteris paribus*, directly proportional to the absorption coefficient of the gas, and inversely proportional to the square root of its density (Exner, Sitzungsber. Akad. Wiss. Wien, 1874, 70, ii. 465; *cf.* Müller, Ann. Physik, 1891, 43, 554). Other workers, who have studied the diffusion of gases through a jelly, through a layer of water supported by a plate of hydrophane, or through a rubber membrane, find that Exner's law is only an approximate statement of the facts (*see* Wroblewsky, Pogg. Ann. 1876, 158, 545; Ann. Physik, 1879, 8, 29; Hüfner, Zeitsch. physikal. Chem. 1898, 27, 227; Hagenbach, Ann. Physik, 1898, 65, 673). Except for oxygen, the diffusion coefficients of gases are smaller in gelatine solution than in pure water. •

Diffusion of Dissolved Substances.

The foundation of our knowledge of this subject was laid by the classical experiments of Thomas Graham (*see* Chemical and Physical Researches, pp. 444–600). In his experiments, 700 cub. cm. of water were placed in a cylindrical jar, and then 100 cub. cm. of the solution to be diffused were carefully conveyed to the bottom of the jar by a pipette. After a suitable time, portions of 50 cub. cm. were successively drawn off; these portions were evaporated, and the amount of substance that had diffused into each layer was thus ascertained. Graham's comparative experiments on the diffusive power of different substances in aqueous solution led him to draw a distinction, which has become of the highest importance, between the behaviour of easily crystallisable substances, and that of substances which are marked by the absence of the power to crystallise. So far as diffusibility is concerned, the distinction in question is based on the following figures, representing approximate times of equal diffusion : hydrochloric acid, 1; sodium chloride, 2·3; sucrose, 7; magnesium sulphate, 7; albumin, 49; caramel, 98. The difference in diffusive power of crystalloids and colloids is very evident from these figures.

The significance of the quantitative results obtained by Graham was emphasised by Stefan (Sitzungsber. Akad. Wiss. Wien, 1878, 78, ii. 957; 1879, 79, ii. 161), who showed that they were in harmony with Fick's diffusion law; that is, the diffusion of substances in aqueous solution is comparable with the distribution of heat in conductors. Fick's law is expressed algebraically by the formula $dS = -kq\frac{dc}{dx}dt$, where dS is the amount of substance crossing a section of the diffusion column in time dt, the sectional area of this column being q sq. cm., and dc/dx being the concentration gradient; k is known as the 'diffusion coefficient.'

The diffusion of dissolved substances, notably electrolytes, has been the subject of repeated investigation, but the method employed has not differed materially from that of Graham, described above (*see* Scheffer, Zeitsch. physikal. Chem. 1888, 2, 390; Arrhenius, *ibid.* 1892, 10, 51; Abegg, *ibid.* 1893, 11, 248; Euler, Ann. Physik, 1897, 63, 273; Abegg and Bose, Zeitsch. physikal. Chem. 1899, 1, 17; Thovert, Compt. rend. 1902, 134, 826; Graham, Proc. Roy. Soc. 1903, 72, 212; Oholm, Zeitsch. physikal. Chem. 1904, 50, 309). The general result of these investigations has been to substantiate the validity of Fick's law, although the opposite opinion also has been expressed (*see* Wiedeburg, Zeitsch. physikal. Chem. 1892, 10, 509).

Special interest has attached to the diffusion of electrolytes since the enunciation of Arrhenius's dissociation theory, according to which the ions of an electrolyte in aqueous solution are to be regarded in many respects as separate units. The researches of Kohlrausch have proved that the contribution which the one ion of an electrolyte makes to the equivalent conductivity is independent of the other ion associated with it, and Nernst has shown that the mobility which is thus characteristic of each ion must be a determining factor in the diffusive power of any electrolyte of which the ion forms a part (Zeitsch. physikal. Chem. 1888, 2, 613). He has further deduced a theoretical relationship between the diffusion coefficient of a binary electrolyte and the conductivities of the two ions, and the values of the diffusion coefficient calculated on this basis are in good agreement with the results of experimental work.

By allowing substances to diffuse into a jelly the effects of convection currents and mechanical disturbances are eliminated and the difficulties attending the experimental study of liquid diffusion are diminished. The rate of diffusion is, at most, very slightly lower in a jelly than in water at the same temperature. Experiments, in which the ends of cylinders of agar-agar jelly were immersed in aqueous solutions of various substances, have shown that the total amount of substance diffusing into the jelly is proportional to the square root of the time during which diffusion has taken place. This is a result in harmony with Fick's law (*see* Voigtländer, Zeitsch. physikal. Chem. •1889, 3, 316; *cf.* Chabry, Journ. de Physique, 1888, 7, 115; Morse and Pierce, Zeitsch. physikal. Chem. 1903, 45, 589; Hausmann, Zeitsch. anorg. Chem. 1904, 40, 110).

Experiments have been made also on the diffusion of various electrolytes and non-electrolytes in alcohol (Kawalki, Ann. Physik, 1894, 52, 166, 300; 1896, 59, 637), of various metals in mercury, fused lead, &c. (Meyer, *ibid.* 1897, 61, 225; 1898, 64, 752; Humphreys, Chem. Soc. Trans. 1896,·69, 243, 1679; Roberts-Austen, Phil. Trans. 1896, 187, 383; von Wogau, Ann. Physik, 1907, 23, 345), and of chlorine, bromine, and iodine in some organic solvents (Euler, Ann. Physik, 1897, 63, 273; Walden, Zeitsch. Elektrochem. 1906, 12, 77). In the last-mentioned connection, Walden has shown that, when a given halogen is considered, the product 'diffusion coefficient × viscosity of solvent ' is a constant, independent of the nature of the solvent. The value of the product for the different halogens is inversely proportional to the square root of the molecular

weight (cf. Pissarjewsky and Karp, Zeitsch. physikal. Chem. 1908, 63, 257).

The different rates of diffusion found by Graham for different substances suggested to him that the process of diffusion might be useful in separating the constituents of an aqueous solution. In this connection, he found that the difference in diffusive power between crystalloids and colloids, referred to above, was greatly accentuated by the interposition of a colloid membrane between solution and solvent, and the method of separation by diffusion through a septum of gelatinous matter he termed ' dialysis.' A sheet of parchment paper, for instance, is tied tightly over the end of a cylindrical or bell-shaped glass vessel, provided with a flange, and into the receptacle so formed, a ' dialyser,' as it is called, the mixed solution of crystalloids and colloids is poured. The outside of the parchment membrane is bathed with water, which is frequently renewed, and the result is that the contents of the dialyser, after a few days, are found to be practically free from crystalloids. Instead of the apparatus just described, a sausage-skin dialyser may be employed : the parchment tube is charged with the solution of crystalloid and colloid, and is hung up by its ends in a vessel of water.

Collodion may be used as a membrane instead of parchment, and it is obtainable in any desired form by the evaporation of the ordinary collodion solution (see Lillie, Amer. J. Physiol. 1907, 20, 127 ; Schryver, Proc. Physiol. Soc. 1908, 23).

Dialysis plays a considerable part in the technical production of beet sugar. In the diffusion process for the extraction of the sugar, beet cuttings are treated with hot water. Such treatment kills the protoplasm, and the cell membrane, which in the living state is impermeable to sugar, now allows this substance to pass out into the water. The high temperature also favours rapid diffusion. The albuminous substances in the beet juice, however, cannot readily penetrate even the dead protoplasm, which acts as a differential membrane, and thus leads to a dialytic separation of the sugar from some of the non-sugar constituents of the cell sap. In the treatment also of beet sugar molasses dialysis with parchment membranes is employed. The result of this procedure is to reduce the salt content of the molasses, and so make possible the crystallisation of a further portion of the sugar (v. SUGAR).

Diffusion of Solids.

The efficiency of certain cementation processes indicates that one solid can slowly penetrate another. The occurrence of diffusion in solids has been proved by experiment of Roberts-Austen (Phil. Trans. 1896, 187, 383), who finds that at temperatures between 100° and 200° there is an appreciable diffusion of gold into solid lead in 30 or 40 days, although the penetration is much slower than into the fluid metal. Experiments lasting over four years have shown that gold diffuses into solid lead, even at the ordinary temperature (Roberts-Austen, Proc. Roy. Soc. 1900, 67, 101).

J. C. P.

DIFORMIN v. FORMINS. •

DIGALENv. DIGITALIS and SYNTHETIC DRUGS.

DIGALLIC ACID (*Gallotannic acid, tannin*) v. TANNIC ACIDS.

DIGESTER v. AUTOCLAVE.

DIGIFOLIN, DIGIPAN, DIGITALEÏN, DIGITALIN, DIGITALOSE, DIGITALYSATUM, DIGITOFLAVONE, DIGITONIN, DIGITOPHYLLIN, DIGITOXOSE v. DIGITALIS.

DIGIPOTENE. A preparation of digitalis leaves.

DIGIPURATUM v. DIGITALIS.

DIGITALINUM VERUM v. DIGITALIS.

DIGITALIS. *Foxglove. Digitalis folia*, B.P. *Digitalis*, U.S.P. (*Digitale*, Fr. ; *Fingerhut*, Ger.) The foxglove, *Digitalis purpurea* (Linn.), had been for some centuries a popular remedy for dropsy, when it was introduced into scientific medicine by Withering, about 1775. It is principally used for its action on the heart ; it slows the beats, and makes them more powerful and regular, so that the output is increased. Only the leaves are official ; the seeds have a similar action, due, however, to different principles. •

Foxglove is a biennial plant, and the Brussels conference agreed that only the second year's leaf should be used ; but, except for the greater difficulty of identification, there is no objection to using the first year's rosettes, which are as good as the flowering plant (Straub, Arch. Pharm. 1917, 255, 198). Cultivated plants up to the beginning of the flowering period, are fairly constant in activity ; variations appear when the seeds ripen. It would probably be the more economical to cultivate only first-year plants. Mature wild plants differ greatly in various localities (Straub). The time for gathering these is July and August, the British Pharmacopœia prescribes leaves from plants beginning to flower. For further detail, see Nativelle (J. Pharm. Chim. [iv.] 20, 81), and for culture, harvesting, and conservation, Newcomb (Amer. J. Pharm. 1912, 84, 201). For *D. Thapsi*, which has a similar action to *D. purpurea*, but is three times as strong, see Farwell and Hamilton, Amer. J. Pharm. 1917, 89, 147.

The active principles of *digitalis* (as of other plants with a like action, such as *strophanthus* and *squill*) are complex glucosides, often amorphous, and this explains the great difficulties and numerous contradictions with which the chemistry of *digitalis* is beset. The confusion is increased by the use of the same name (digitaline) for different substances, and by the application of different names to the same substance. According to our present knowledge, cold water extracts from the leaves a mixture of glucosides, but hardly dissolves digitoxin, which may be subsequently extracted by alcohol. From the aqueous extract chloroform removes the ' gitalin ' fraction, and leaves behind one or more glucosides, designated as the ' digitaleïn ' fraction, which is less active than either gitalin or digitoxin, and has not been obtained even approximately pure. Historically, the first moderately pure, but amorphous, active preparation was ' *digitaline* ' of Homolle (J. Pharm. Chim. 1845, [iii.] 7, 57), undoubtedly a mixture. Nativelle (J. Pharm. Chim [iv.] 1869, 9, 225 ; 1872, 16, 430 : 1874, 20, 81) later prepared a • *digitaline cristallisée,*' a commercial specimen of which Schmiedeberg

(Arch. exp. Path. Pharm. 1874, 3, 16) declared to consist very largely of a substance to which he gave the name *digitoxin*, and as this substance was afterwards principally investigated in Germany, under this name, Nativelle's designation has been displaced, in spite of French protests (*e.g.* Arnaud, Compt. rend. 1889, 109, 679) Kiliani, who has published something like forty papers on the chemistry of digitalis (Ber. 1890, 23, 1555 to 1918, 51, 1613 ; and Arch. Pharm. 1892, 230, 250 to 1916, 254, 255), at one time did not agree with the identification of Nativelle's digitaline with Schmiedeberg's digitoxin, and considered the former substance identical with a crystalline leaf glucoside described by himself as *digitophyllin* (Arch. Pharm. 1897, 235, 425). Later, Kiliani (Ber. 1898, 31, 2454) considered digitaline cristallisée and digitoxin very closely similar, but doubtfully identical. An attempt to restore the historically correct name for this glucoside would lead to still greater confusion, especially as German writers mean by digitalin a totally different glucoside from the seeds.

The 'gitalin' fraction is, on account of its solubility in water and its physiological action, probably of most importance therapeutically ; it was little studied until Kraft (Schweiz. Wochenschr. Chem. Pharm. 1911, 49, 161, 173, 236 ; Arch. Pharm. 1912, 250, 118) described the isolation of a crystalline glucoside *gitalin*. Kiliani (Arch. Pharm. 1914, 252, 13) has declared Kraft's preparation to be a mixture, but in any case it contains one or more crystalline substances of great activity, having the advantage over digitoxin of solubility in water, at least in the crude state. Indeed, the gitalin fraction seems to have been utilised some years before Kraft by Cloetta (Muench. mediz. Wochenschr. 1904, 51, 1466), whose 'digitoxinum soluble' is not digitoxin in a water soluble form (Kiliani, Ber. 1907, 40, 2996), but consists largely of gitalin (Gottlieb, *e.g.* Arch. exp. Path. Pharm. 1918, 83, 117).

For the preparation of their substances, both Homolle and Nativelle extracted the powdered leaves with 50 p.c. alcohol, and purified the extract with lead acetate. After removal of the excess of lead, Homolle evaporated to a syrup and precipitated in the cold with tannic acid. The tannic acid precipitate was washed with tepid water, mixed with an equal weight of lead oxide, dried, and extracted with 90 p.c. alcohol. After treatment with charcoal and evaporation, the residue was extracted with ether to remove impurities. Tannin, apparently introduced by Homolle, was later applied to the separation of *k*-strophanthin (*q.v.*), and seems to be still in use for such commercial preparations as digipuratum (*see* below) ; but it is, of course, only a general colloidal precipitant, and cannot be expected to act specifically. Nativelle moistened the powdered leaves with a solution of neutral lead acetate, then extracted with 50 p.c. alcohol, and purified the extract repeatedly with charcoal and lead acetate. He finally extracted with chloroform, and thus separated off the 'digitalein' fraction, which enabled him to obtain a crystalline substance. Schmiedeberg (*l.c.*) introduced the preliminary extraction of the leaves with cold water, thus removing the gitalin and digitalein fractions,

and then, after pressing the leaves, he extracted with 50 p.c. alcohol. After precipitation with basic lead acetate, and removal of the excess with ammonia, the alcohol was evaporated, while the solution was kept neutral. A partly crystalline substance separated, which was dried on the water-bath and extracted with chloroform. The residue, after evaporation of the chloroform, was washed with ether (which removes fat, luteolin, &c.), or with boiling petroleum ether, and then crystallised the digitoxin from 80 p.c. alcohol with charcoal. Kiliani's method of preparing digitoxin (Arch. Pharm. 1895, 233, 311) is similar.

Digitaline cristallisée, Digitoxin $C_{34}H_{54}O_{11}$ (Kiliani) forms hydrated needles and leaflets from aqueous alcohol, which become anhydrous and sinter at 145°-150°, and anhydrous prisms from methyl alcohol and chloroform, melting at 245° (243°-245° Arnaud). Kraft (Arch. Pharm. 1912, 250, 418) could not obtain the hydrated form, and concludes Kiliani's supposed hydrate was contaminated with gitalin.

The yield of digitoxin is said to be 0·1 p.c. of the leaves, but Straub (*l.c.*) has concluded from physiological evidence that the amount present is very variable, and may considerably exceed 0·1 p.c. Merck's commercial preparation is stated by Kiliani to be about 90 p.c. pure. 0·65 gram digitaline (digitoxin) dissolves at 14° in 100 c.c. absolute alcohol (Arnaud). Digitoxin dissolves readily in chloroform, only slightly in ether, not in water. It gives a characteristic colour reaction ; glacial acetic acid and concentrated sulphuric acid are employed, 100 c.c. of each being previously diluted with 1 c.c. of 5 p.c. aqueous ferric sulphate solution. A trace of digitoxin is dissolved in 1 c.c. of the acetic acid, and 2 c.c. of the sulphuric acid are allowed to flow underneath, in a narrow test tube. The zone of contact becomes dirty brown, and after a few minutes the acetic acid begins to become indigo blue. This, Keller's reaction, is still positive with 0·1 mg. in 1 c.c. of acetic acid. Concentrated hydrochloric acid dissolves digitoxin in the cold to a colourless solution, becoming bluish-green on warming. Alcoholic sodium hydroxide hydrolyses to *digitoxinic acid* $C_{34}H_{56}O_{12}$, mineral acids hydrolyse to two molecules of *digitoxose*

$$CH_3 \cdot CHOH \cdot CHOH \cdot CHOH \cdot CH_2 \cdot CH \cdot O$$
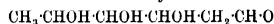
m.p. 101°, and one of *digitoxigenin* $C_{22}H_{32}O_4$, m.p. 230° (*v. e.g.* Kiliani, Arch. Pharm. 1913, 251, 562). Digitoxose is a peculiar sugar, and gives Keller's reaction, digitoxigenin does not.

Gitalin $C_{28}H_{46}O_{10}$ (?), m.p. 150°-155°, is amorphous, and was obtained by Kraft by a method analogous to that of Homolle (*v. supra*), and extracting the glucoside from aqueous solution by shaking with chloroform ; after drying, the chloroform solution is precipitated by light petroleum. Gitalin is soluble in 600 parts of water, and very readily in chloroform. By dissolving in 1·5 parts of alcohol and adding 0·75 part of water, a crystalline *gitalin hydrate* $C_{28}H_{46}O_{10}, 4H_2O$, m.p. 75°, is separated. Solutions of gitalin deposit on keeping mixtures of gitalin and *anhydrogitalin* $C_{28}H_{46}O_9$, m.p. 255°, crystallising from dilute alcohol and almost insoluble in chloroform. On hydrolysis by acids, gitalin, its hydrate, and its anhydride all

yield digitoxose (see above), and hence they all give Keller's reaction; the other fission product is anhydrogitaligenin $C_{22}H_{24}O_5$, m.p. 216°–219°, crystallising from alcohol. As already stated, Kiliani considers gitalin to be a mixture, of anhydrogitalin with other substances, but this does not dispose of Kraft's contribution to the subject.

Digitaleïn (Schmiedeberg) differs from gitalin and digitoxin in not producing the typical systolic arrest of the heart.

Commercial Preparations of Digitalis.—A considerable number of these have been introduced of late years, mostly in Germany. Digalen (Hoffmann-Laroche & Co.), introduced in 1904, has been one of the most successful. It is Cloetta's 'digitoxinum solubile'=impure gitalin? (see above). Digifolin and digipan are similar impure active principles. Digipuratum (D. R. P 227552, 245193, 246571, of Knoll & Co.) is a purified leaf extract freed from digitonin, and apparently consists of the tannin compounds of the gitalin fraction. From adigan the digitonin has been removed by cholesterol (see below). Digitalysatum, from fresh press-juice, and other preparations, are purified by dialysis. Digitalone (Parke, Davis & Co.) is a sterile extract of older type. For a physiological examination of these preparations, see Rapp, Pharm. Zentral-H 1914, 55, 961, 978. ·

Methods of Assay.—There is a great variation in the content of active leaf glucosides. Thus Straub (l.c.) found, in percentages of the air-dry leaf :—

Gitalin + digitalein, cultivated, 0·4–0·64, wild, 0·22–0·89 ; digitoxin, cultivated, 0·053–0·11, wild, 0·01–0·15.

This variability has led to the introduction of standardised leaves (' folia digitalis titrata ') and to methods of assay of pharmaceutical preparations (official in the U.S.P. for digitalis, strophanthus, and squill). A chemical assay (of digitoxin ?) has been described by Keller (Ber. Deut. pharm. Ges. 1897, 7, 125), but Ziegenbein (Arch. Pharm. 1902, 240, 454) has shown that there is no relation between physiological activity and the ' digitoxin ' found by Keller's method. Barger and Shaw (Pharm. J. 1904, [iv.] 19, 249) have confirmed this, and shown that of added crystalline digitoxin less than half is recoverable by Keller's method. The chloroform extract, weighed in this method, consists, according to Kraft (l.c.), largely of gitalin. The assay must therefore be physiological, and is generally based on Houghton's method (J. Amer. med. Assoc. 1898), by which the minimum amount is determined necessary to arrest the frog's heart in systole, in, say, 1 hour (for length of time, cf. Gottlieb, below). The isolated frog's heart may also be employed, with graphic registration of its action (Schmiedeberg, Arch. exp. Path. Pharm. 1910, 62, 307). For earlier investigations, see Edmunds and Hale (Bull. No. 48, Hygienic Lab. Washington, 1909) and Focke (Arch. Pharm. 1910, 248, 365) ; for the later ones, Holste (Zeit. exp. Path. Ther. 1917, 19, 153), Focke (ibid. 1914, 16, 443), Straub (Arch. exp. Path. Pharm. 1916, 80, 52), and Gottlieb (ibid. 1918, 83, 117). The susceptibility of frogs is greater in winter than in summer, and it has been suggested that they should themselves be standardised with a pure sub-

stance, such as digitoxin (Rapp, l.c.), or g-strophanthin (ouabaïn) (q.v.), suggested by Heinz, and adopted by the U.S.P. This presupposes a constant ratio of sensitiveness to dissimilar preparations, which has not been proved. Indeed, Gottlieb (l.c.) states that the sensitiveness of frogs to g-stropanthin is fairly constant throughout the year.

Digitalis seeds contain entirely different glucosides, which have been examined chiefly by Kiliani. From an alcoholic extract, purified with lead acetate, the mixed glucosides' are precipitated with tannic acid (cf. Homolle's method). This gives the commercial so-called digitalinum germanicum, which may be separated, according to Kiliani (Ber. 1918, 51, 1613), into ' digitalinum verum,' or digitalin, digitonin, gitonin, and a fourth glucoside.

Digitalin $C_{75}H_{56}O_{14}$, m.p. 210°–217°, is less active than digitoxin, and forms amorphous granules, soluble in 1000 parts of water. It dissolves in sulphuric acid with a yellow colour, which, on standing, or in the presence of ferric salts or other oxidising agents, becomes cherry-red and purple. It is hydrolysed by acids to equimolecular proportions of glucose, digitalose $C_7H_{14}O_5$, and digitaligenin $C_{22}H_{30}O_3$, needles, m.p 210°–212°. Digitalose is a syrup, and is oxidised by nitric acid to methoxydihydroxyglutaric acid (Kiliani, Ber. 1905, 38, 3622 ; 1916, 49, 709).

Digitonin $C_{54}H_{92}O_{28}$ or $C_{55}H_{91}O_{28}$, m.p. 225°–235°, $[\alpha]_D = -49·25°$, is obtained in the crude state in a yield of about 45 p.c. of the ' German digitalin' employed. It is important as an example of a crystalline saponin, and probably also occurs in the leaves. It has no stimulant action on the heart, and is therapeutically undesirable. Digitonin dissolves to a clear solution in 50 parts of cold 50 p.c. alcohol, is more soluble on heating, and crystallises on cooling in fine needles. It is hardly soluble in chloroform, and forms an opalescent solution in water, which froths. Keller's reaction is negative. Acids hydrolyse to two molecules of glucose, two of galactose, and one of digitogenin $C_{30}H_{48}O_4$ or $C_{31}H_{50}O_4$, needles, m.p. 240°. Like other saponins, digitonin combines with cholesterol. On mixing a (preferably hot) solution of 1 gram digitonin in 100 c.c. of 90 p.c. alcohol with 0.4 gram cholesterol in 60 c.c. of 95 p.c. alcohol, the addition compound $C_{55}H_{94}O_{28} \cdot C_{27}H_{46}O$ crystallises (Windaus, Ber. 1909, 42, 238). Similar compounds with lower alcohols and phenol had already been observed by Houdas (Compt. rend. 113, 648). This reaction has met with wide application. On the one hand, digitonin can be removed from digitalis preparations (adigan, above), on the other hand, sterols can be estimated in fats, for as little as 0·1 mg. of cholesterol in 1 c.c. of 90 p.c. alcohol may be detected (Windaus). (Cf. Panzer, Zeitsch. physiol. Chem. 1912, 78, 414 ; Marcusson and Schilling, Chem. Zeit. 1913, 87, 1001 ; Berg and Angershausen, ibid. 1914, 38, 978 ; Prescher, Zeitsch. Nahr. Genussm. 1914, 33, 7.)

Gitonin.—Commercial digitonin (Merck) contain 5–14 p.c. of a closely similar glucoside gitonin $C_{49}H_{80}O_{23}, 7H_2O$, m.p. 225° (Kraft, l.c. ; Windaus and Schneckenburger, Ber. 1913, 46, 2628), which may be crystallised (Kiliani, ibid.

1916, 49, 701), and also forms cholesterol addition compounds.

Straub (Biochem. Zeitsch. 1917, 82, 48) finds that on germination the first pair of foliage leaves already contains the typical leaf glucosides, and in 4 months the maximum of 1 p.c. of total glucoside is already nearly attained. This is made up of gitalin fraction, $\frac{1}{5}$ p.c. ; digitalein fraction, $\frac{1}{4}$ p.c. ; and digitoxin fraction, $\frac{1}{4}$ p.c. For variations, see above.

Digitalis leaves contain *luteolin* (='*digito-flavone*') $C_{15}H_{10}O_6,H_2O$, which imparts a yellow colour to ethereal extracts (Kiliani and Mayer, Ber. 1901, 34, 3577).

Other Drugs with a Digitalis-like Action.— Schmiedeberg (Arch. exp. Path. Pharm. 1883, 16, 149, especially 162) has enumerated a considerable number of these. Strophanthus and squill (*q.v.*) are therapeutically the most important ; *see* also euonymus, hellebore, and the alkaloid erythrophlœine.

Cymarin, a glucoside from the root of *Apocynum cannabinum* has been obtained crystalline (D. R. P. 255537, of · Bayer & Co.) 1000 parts of the root are extracted with boiling carbon tetrachloride until no ,longer bitter. After evaporation, the residue is dissolved in 1000 parts of alcohol, and water at 50° is added, until no more resin is precipitated. After filtration, basic lead acetate is added, and the excess of lead is removed, after a second filtration, by means of hydrogen sulphide. After evaporation to 100 parts, the solution is extracted with chloroform, and the chloroform dried with sodium sulphate. Impurities are then precipitated with ether, and next the cymarin with light petroleum. It is·crystallised from methyl alcohol, and then has the composition :

$$C_{30}H_{44}O_9,CH_3OH,\tfrac{1}{2}H_2O$$
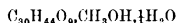
$[a]_D^{20}=+23\cdot5°$ in chloroform. It gives Liebermann's cholesterol reaction (*v.* STROPHANTHIDIN), and Keller's digitoxin reaction (above),‿and is hydrolysed by acids

$$C_{30}H_{44}O_9+H_2O=C_{23}H_{30}O_5,H_2O+C_7H_{14}O_4$$
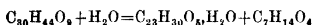
into cymarigenin (=strophanthidin, *q.v.*) and cymarose, which is probably the methyl ether of digitoxose (Windaus and Hermanns Ber. 1915, 48, 979), where the earlier investigations on *Apocynum* are referred to.

Bufagin $C_{18}H_{24}O_4$, from the parotid gland of the Central-American toad *Bufo aqua*, has also been obtained crystalline and pure (Abel and Macht, J. Pharm. exp. Therap. 1912, 3, 319). It is not a glucoside. For *bufotalin* from European toads, *see* Wieland and Weil (Ber. 1913, 46, 3315).

Convallamarin $C_{23}H_{44}O_{12}$ and *convallarin* $C_{34}H_{62}O_{11}$ are crystalline glucosides from *Convallaria majalis* (Linn.) (Lily of the Valley), which plant was deleted from the U.S.P. in 1916 (Walz, Jahrb. f. Chem. 1858, 518).

‍ *a-Antiarin* $C_{27}H_{42}O_{10},4H_2O$ and *β-antiarin* are crystalline glucosides from the latex of *Antiaris toxicaria*, the Upas tree of Java (Kiliani, Ber. 1910, 43, 3574). Other crystalline glucosides with digitalis action are *thevetin* $C_{54}H_{84}O_{24}$, from the seeds of *Thevetia neriifolia* (Juss.), crystallising readily (de' Vrij, Pharm. J. 1881, 457 ; Warden, *ibid.* 1881, 417), and *echujin*

$(C_8H_9O_2)n$, from the latex of *Adenium Bœhmianum* (Schinz), a South-West African arrow poison (Boehm, Arch. exp. Path. Pharm. 1899, 26, 165). The latter substance has an activity intermediate between that of digitoxin and strophanthin.

Tanghinin $C_{27}H_{46}O_8$, m.p. 182°, from the fruits of *Tanghinia venenifera* (Madagascar), is crystalline, hardly soluble in water, readily in alcohol and in ether, and is not a glucoside (Arnaud Compt rend. 1889, 108, 1255). *Adonin* $C_{24}H_{40}O_9$, from *Adonis amurensis* (Reg. et Radd.) (Tahara, Ber. 1891, 24, 2579), *adonidin* from *A. vernalis* (Linn.) (Cervello, Arch. exp. Path. Pharm. 1882, 15, 235), and *oleandrin* from *Nerium oleander* (Linn.) (Schmiedeberg, *l.c.*) are amorphous. Many of the above substances are used as arrow poisons. The N.O. *Apocynaceæ* seems to be especially rich in substances with a digitalis-like action (*Apocynum, Strophanthus, Thevetia, Adenium, Nerium oleander*). Windaus and Hermanns (Ber. 1915, 48, 981) have suggested that there is a more or less close chemical relationship between many of the above substances The non-sugar portion of the glucosides (' genin ') seems to be derived from a cholesterol-like complex by various degrees of oxidation ; the sugars are peculiar and sometimes identical or closely related, and often contain less oxygen than carbohydrates. The genins are less active than the glucosides (*v. k*-strophanthin and Straub, Biochem. Zeitsch. 1916, 75, 132). G. B.

DIGITALON *v.* DIGITALIS.

DIGITOXIN *v.* DIGITALIS.

DIHEPTYLACETIC ACID $(C_7H_{15})_2CH\cdot COOH$ is obtained by treating diheptylacetoacetic ester with potassium hydroxide (Jourdan, Annalen, 200, 116) ; m.p. 26°-27°.

DIHYDRAZINES *v.* HYDRAZINES.

DIHYDROCAMPHOKETONE *v.* KETONES.

DIHYDROXY- ACIDS *v.* HYDROXY- ACIDS.

DIHYDROXYANTHRAQUINONES. *See* ALIZARIN AND ALLIED COLOURING MATTERS.

DIHYDROXYBENZOIC ACIDS *v.* PROTO-CATECHUIC ACID.

DIHYDROXYCARBOXYNAPHTHALENE SULPHONIC ACIDS. *See* NAPHTHALENE.

5 : 5'-DIHYDROXY-7 : 7'-DISULPHO-2 : 2'-DINAPHTHLY CARBAMIDE
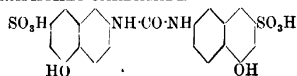
Prepared by the action of carbonyl chloride upon an aqueous solution of 2-amino-5-naphthol-7-sulphonic acid containing sodium carbonate, acidifying with hydrochloric acid, and adding common salt (Farbenf. vorm. F. Bayer & Co., D. R. P. 116200).

1 : 5-DIHYDROXYNAPHTHALENE. *See* NAPHTHALENE.

DIHYDROXYNAPHTHALENE SULPHONIC ACIDS. *See* NAPHTHALENE.

DIHYDROXYTARTARIC ACID

$$CO_2H\cdot C(OH)_2\cdot C(OH)_2\cdot CO_2H$$
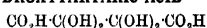
is made by the action of a mixture of fuming sulphuric acid and nitric acid upon dry tartaric at 20°, cooling with ice and neutralising with sodium carbonate when the sparingly soluble sodium salt separates out. Used in making

tartrazine : *v.* PYRAZOLONE COLOURING MATTERS and KETONES.

DI-IODOFORM *v.* SYNTHETIC DRUGS.

DIKA-BREAD. An edible cake made by the natives of Sierra Leone and the Gaboon from the fruit of the mango tree, indigenous to most tropical climates. The fruit resembles chocolate in appearance, and contains a large quantity of fatty matter. It has occasionally ripened under hot-house cultivation in this country.

DIKA FAT GROUP. Under this name may be comprised several fats which are characterised by high saponification values, like the fats of the Cocoa Nut Oil group, but which differ from them by the absence of volatile fatty acids. The high saponification value indicates a preponderant proportion of lauric acid. These fats are further characterised by low iodine values. The most prominent of this group are · (1) **Dika fat**, obtained from the seed-kernels of various kinds of *Irvingia* : *I. gabonensis* (Baill), *I. Barteri* (Hook, fl.), indigenous to West Africa. The seeds yield about 65 p.c. of a yellowish-white fat, which the natives separate by expressing the kernels after boiling with water. The fat melts at about 30°, and has an iodine value of about 31. (2) **Tangkallak fat**, obtained from the fruits of *Lepidadenia Wightiana* (Nees : Bl.), *Cylicodaphne sebifera* (Bl), *Tetranthera calophylla* (Miquel), *Tetranthera laurifolia* (Jacq.), *Litsea Sebifera* (Pers.), *Sebifera glutinosa* (Lour) (3) **Irvingia butter. Cochin-China wax,** or **Cáy-cáy fat**, the fat obtained from *Irvingia Oliveri* (Pierre), *Irvingia malayana* (Oliv.), *Irvingia Harmandiana* (Pierre), *Buchanania fastigiata* (H Baillon). The Cáy-cáy tree—' candle tree '—is a tropical tree indigenous to Cochin China and Cambodia. Large quantities of the fat are used by the natives as candles. The freshly prepared fat is employed for edible purposes. (4) **Kusu oil**, contained in the fruit of the camphor-yielding tree, *Cinnamomum camphora* (Nees), *Lauraceæ*. From its chemical characteristics, the conclusion may be drawn that it consists of pure laurin with a few per cent. of olein.   J. L.

DIKETONES *v.* KETONES.

DIKETOSUCCINIC ACID *v.* KETONES

DILATOMETER. A term originally used to denote an apparatus for measuring the thermal expansion of liquids. Subsequently given by Silbermann to an instrument for determining the strength of aqueous alcohol.

DILITURIC ACID, *nitrobarbituric acid, nitromalonylurea,* $CO\underset{NH\cdot CO}{\overset{NH\cdot CO}{<}}CH\cdot NO_2, 3H_2O$, obtained by treating alloxantin first with hydrochloric acid and subsequently with nitric acid (Schlieper, Annalen, 56, 24); by warming hydurilic acid with nitric acid (Baeyer, *ibid.* 127, 211); by nitrating barbituric acid with fuming nitric acid (Baeyer, *ibid.* 130, 140); by oxidising violuric acid (nitrosobarbituric acid) (Ceresole, Ber. 16, 1134); or by oxidising with nitric acid the compound $C_{16}H_{28}O_{11}N_{12}S_2$ obtained by condensing *iso*dialuric acid with thiocarbamide (*v.* Vogel, Annalen, 315, 259; Bartling, *ibid.* 339, 27).

Dilituric acid crystallises in colourless quadratic prisms or plates, is sparingly soluble in cold, more readily so in hot water, is sparingly soluble in alcohol and insoluble in ether. It

forms chloropicrin when warmed with bleaching powder, is reduced by hydriodic acid to *uramil (aminobarbituric acid)*, and suffers partial reduction when heated with glycerol, yielding *violuric acid*. Dilituric acid is tribasic, but most of the salts are acidic, and contain only one equivalent of the metal; they are sparingly soluble in water, and are not generally decomposed by mineral acids. The *ammonium salt*

$$C_4H_2(NH_4)O_5N_3$$

the *sodium salt* $C_4H_2NaO_5N_3, 4H_2O$, *potassium salt* $C_4H_2KO_5N_3$, *calcium salt*

$$Ca(C_4H_2O_5N_3)_2, 4H_2O$$
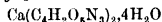
the *barium compound* $BaCl(C_4H_3O_5N_3), H_2O$, *ferrous salt* $Fe(C_4H_2O_5N_3)_2, 8H_2O$, and the *silver salt* $C_4H_2AgO_5N_3, 2H_2O$, are colourless; the *ferric salt* $Fe(C_4H_2O_5N_3)_3, 6H_2O$ is bright yellow, the *copper salt* $Cu(C_4H_2O_5N_3), H_2O$ is greenish, the *dipotassium salt* $C_4HK_2O_5N_3$ is bright-yellow (Schlieper, *l.c.*), and the *truargentic salt* $C_4Ag_3O_5N_3$ is lemon-yellow (Baeyer, Annalen, 130, 140). According to Holleman (Rec. trav. chim. 1897, 16, 162), dilituric acid and its homologues are aliphatic nitro- compounds in which the *iso-* form (*cf.* Hantzsch and Schultze, Ber. 1896, 29, 699, 2251; Hantzsch and Veit, *ibid.* 1899, 32, 607) is the stable modification. The aqueous solution of dilituric acid is faintly yellow and decomposes carbonates; the molecular conductivity for 1 gram-molecule dissolved in *v* litres of water is 323·4 (*v*=32), 341·4 (*v*=512), (μ_∞ should be 356); the acid is therefore almost completely dissociated in aqueous solution; the addition of one equivalent of a base does not appreciably change the colour of the solution, but on adding a second equivalent, the solution assumes the deep-yellow colour characteristic of the aqueous solutions of the salts of this acid. Assuming that the formula $CO\underset{NH\cdot CO}{\overset{N=C(OH)}{<}}\rangle C\cdot N\cdot OH$ represents the constitution of the acid, Holleman states that the anion

$$CO\underset{NH\cdot CO}{\overset{N=C(O-)}{<}}\rangle C\cdot N\cdot OH$$
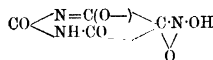
is colourless and slowly hydrolyses into the yellow anion $CO\underset{NH\cdot CO}{\overset{N=C(O-)}{<}}\rangle C\cdot N\cdot O-$.
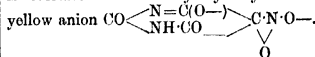
Methyldilituric acid, 1 - *methyl* - 5 - *nitrobarbituric acid* $CO\underset{NH\cdot CO}{\overset{NMe\cdot CO}{<}}CH\cdot NO_2, 1\cdot5H_2O$, prepared by oxidising methylvioluric acid with concentrated nitric acid (Andreasch, Monatsh. 1900, 21, 281), crystallises from aqueous solution, and the anhydrous acid is colourless; it melts and decomposes at 143°, is readily soluble in hot water, less so in cold water, alcohol, or acetone, and sparingly soluble in ether. The aqueous solution of the acid is intensely yellow, and decomposes carbonates; the aqueous solutions of the salts are also yellow, but the solid salts are colourless or pale-yellow and sparingly soluble; the *potassium salt* $C_5H_4KO_5N_3$, the *sodium salt* $C_5H_4NaO_5N_3, H_2O$, the *ammonium salt* $C_5H_4(NH_4)O_5N_3$, are colourless; the *barium salt* $(C_5H_4O_5N_3)_2Ba, H_2O$, the

cadmium salt ($C_5H_4N_3O_5)_2Cd,2H_2O$, are pale-yellow ; the *strontium salt* ($C_5H_4O_5N_3)_2Sr,3H_2O$ is colourless, but becomes yellow on losing its water of crystallisation. Methyldilituric acid is stable with bases ; it reacts readily with chlorine to form *methylchlordilituric acid*

$$CO{<}^{NMe \cdot CO}_{NH \cdot CO}{>}CCl(NO_2)$$
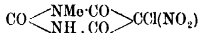
m p. 121° ; the corresponding bromo- compound melts and decomposes at 138°-139°.

Dimethyldilituric acid, 1:3 - *dimethyl* - 5 - *nitro-barbituric acid* $CO{<}^{NMe \cdot CO}_{NMe \cdot CO}{>}CH \cdot NO_2$

obtained by oxidising dimethylvioluric acid with concentrated nitric acid (Techow, Ber. 27, 3085 ; Andreasch, Monatsh. 16, 26) ; forms colourless microscopic crystals from acetone ; dissolves in 5·98 parts of water at 14°, is sparingly soluble in alcohol, melts at 152° and changes into dimethylalloxan (Holleman, Rec. trav. chim. 16, 162), and is reduced by hydriodic acid to dimethyluramil.

Dimethyldiliuric acid is intensely yellow in aqueous solution, and this is due to the presence of the coloured anion of the *isonitro-* form $CO{<}^{NMe \cdot CO}_{NMe \cdot CO}{>}C{:}NO \cdot OH$, for on adding con centrated nitric acid, the colour almost entirely disappears ; further, the molecular conductivity of the acid for 1 gram-molecule dissolved in v litres of water is 313·3 (v=32), and 337·6 (v=1024), (μ_∞ should be 352), so that in each solution the acid is almost completely ionised (Holleman, Rec. trav. chim. 16, 162). The salts of dimethyldiliuric acid are coloured, the *sodium salt* $C_6H_7NaO_5N_3,H_2O$ is yellow, the *potassium salt* $C_6H_7KO_5N_3$ is greenish-yellow, the *magnesium salt* ($C_6H_6O_5N_3)_2Mg,4H_2O$ is yellowish-green, the *calcium salt* ($C_6H_6O_5N_3)_2Ca$ is bluish-green, the *strontium salt* ($C_6H_6O_5N_3)_2Sr$ is pale-green, the *barium salt*

$$(C_6H_6O_5N_3)_2Ba,2H_2O$$
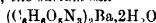
is rose-red, and the *silver salt* $C_6H_6AgO_5N_3$ is greyish-violet (Andreash, *l.c.*, and Monatsh. 21, 295).

Dimethylchlordilituric acid

$$CO{<}^{NMe \cdot CO}_{NMe \cdot CO}{>}CCl(NO_2)$$
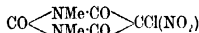
prepared by passing chlorine into an aqueous solution of dimethyldilituric acid ; melts and decomposes at 150° ; the corresponding *bromo-derivative* melts partially at 152° (Andreasch, *l.c.*). Dimethyldilituric acid is readily decomposed by the action of bases forming water, carbon dioxide, and dimethylnitromalonamide.

M. A. W.

DILL FRUIT. *Anethi fructus,* B.P. The dried ripe fruit of *Peucedanum graveolens* (Benth. and Hook.).

DILL OIL v. OILS, ESSENTIAL.

DIMETHYLALLOXAN v. ALLOXAN.

p-**DIMETHYLAMINOBENZOPHENONE** v. KETONES

DIMETHYLAMINONAPHTHAPHENAZINE v. AZINES.

DIMETHYLANILINE $<\!\!\!>\!N(CH_3)_2$.
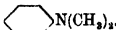
Made by heating a mixture of aniline and methyl alcohol containing sulphuric acid in an autoclave. For details of mode of manufacture,

see Walter, Chem. Zeit. 1910, 34, 641, *et seq.* ; and Cain's Intermediate Products for Dyes. Instead of sulphuric acid iodine may be employed (Knoll & Co., D. R. P. 250236). Or a mixture of aniline and milk of lime and methyl chloride may be heated under pressure (Grandmougin, Rev. prod. chim. 1917, 20, 68).

Dimethylaniline boils at 192·6°/738 mm. ; m.p. 2·07° ; sp.gr. 0·96 at 15° (*see* AMINES).

DIMETHYLDIAMINODI - o - TOLYLME-THANE

$$CH_3 \cdot NH{<}^{CH_3}{>}CH_2{<}^{CH_3}{>}NH \cdot CH_3$$
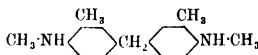
Obtained by treating methyl-*o*-toluidine, or a mixture of mono- and dimethyl-*o*-toluidine with formaldehyde (40 p.c. solution) and hydrogen chloride, diluting with water, adding sodium and steam distilling to expel the excess of the methyl-*o*-toluidine. On cooling the base crystallises, and may be purified by crystallisation from alcohol (Bad. Anil. and Soda Fabrik, D. R. P. 67478) ; m.p. 87° ; b.p. 255°/9 mm.

DIMETHYLDIAMINOTOLUPHENAZINE v. AZINES.

2 : 2'-DIMETHYL-1 : 1'-DIANTHRAQUIN-ONYL
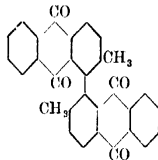
Obtained by diazotising 1-amino-2-methyl-anthraquinone dissolved in sulphuric acid, pouring the product on ice, separating the diazonium sulphate, and treating it with acetic anhydride and copper powder. The precipitate thus formed is mixed with water to remove acetic anhydride, and with dilute nitric acid to free it from copper. Can also be prepared by treating 1-chloromethylanthraquinone with copper powder (Bad. Anilin and Soda Fabrik. D. R. P. 180157) ; m.p. 366°-367°. Used in making Indanthrene Golden yellow. v. Pyranthrene, art. INDANTHRENE.

DIMETHYLETHYL ACETIC ACID v. CA-PROIC ACID.

DIMETHYLGLYOXIME (*βγ-dioximinobutane*) $CH_3 \cdot C : N \cdot OH$
                          | , was originally obtained by
$CH_3 \cdot C \cdot N \cdot OH$
Schramm, in 1883, by acting upon methyl-oximino-ethyl ketone with aqueous hydroxyl-amine hydrochloride (Ber. 16, 180). It is readily prepared in quantity by the following method (Gandurin, J. pr. Chem. 1908, 77, [ii.] 414) :—

850 c.c. of commercial methyl ethyl ketone are mixed with 30 c.c. of hydrochloric acid of sp.gr. 1·19, and 1 litre of amyl nitrite is allowed to run in slowly with vigorous stirring. This takes 1½ hours, and the temperature should be maintained between 40°-50°. When the reaction is over, 800 grams of ice are added, followed by 378 grams of sodium hydroxide in 800 c.c. of water, and the mixture is shaken for half an

hour. After standing, the layer of amyl alcohol is removed, and the aqueous liquid twice extracted with ether. 100 c.c. of the alkaline liquid are treated with the calculated amount of hydroxylamine hydrochloride, and the dimethylglyoxime produced is collected and weighed. If the original volume of the alkaline liquid is v c.c., a grams the weight of dimethylglyoxime obtained from the 100 c.c. of liquid, then the amount of hydroxylamine hydrochloride in grams required for the remaining liquid is equal to $656(v-100)a/109500$. This weight of hydroxylamine hydrochloride is dissolved in a little water, added to the alkaline liquid, and the whole warmed on the water-bath for an hour. The liquid is acidified with acetic acid, and the dimethylglyoxime, which separates, is filtered, washed, and dried. This product is sufficiently pure, but it may, if desired, be recrystallised from alcohol. Yield, 650–700 grams.

(For details, *see* Adams and Kamm, J. Amer. Chem. Soc. 1918, 40, 1281.)

(For other methods of preparation, *v* Biltz, Zeitsch. anal. Chem. 1909, 48, 164 ; Tschugaeff, Ber. 1905, 38, 2520.)

Properties.—Dimethylglyoxime forms colourless, glistening needles, and is insoluble in water, but soluble in alcohol. It melts at 245°–246° (Meyer-Jacobsen, I. (ii.) 826, 1913). Its dibenzoyl derivative forms rhombic plates, melting at 223° (Diels and Stern, Ber. 1907, 40, 1629).

On oxidation with potassium ferricyanide or nitrogen peroxide it yields furoxane (Scholl, Ber. 1890, 23, 3498) ; this is reduced to the dioxime again when treated with zinc and acetic acid (Rimini, Gazz. chim. ital. 1895, 25, [ii.] 266). When heated with aqueous ammonia at 170°–180° it yields the anhydride dimethylfurazan (Wolff, Ber. 1895, 28, 69).

Application in Analysis.—Dimethylglyoxime is now an important analytical reagent, owing to its property of forming a bright scarlet insoluble nickel derivative. It thus becomes possible to estimate nickel simply and accurately, in the presence of iron, aluminium, chromium, cobalt, zinc, or manganese, all of which form soluble derivatives. In addition, an excellent qualitative test for nickel in the presence of cobalt is supplied. For the latter purpose, a pinch of the oxime is added to the solution containing excess of ammonia or sodium acetate, and the liquid boiled. A scarlet precipitate is obtained even when there is present only one part of nickel in two million parts of solution (Tschugaeff, Ber. 1905, 38, 2520 ; Compt. rend. 1907, 145, 679 ; Kraut, Zeitsch. angew. Chem. 1906, 19, 1793). 0·1 milligram of nickel can be detected in the presence of 5000 times as much cobalt.

For the quantitative estimation of nickel, the acid solution is heated nearly to boiling ; a slight excess of 1 p.c. alcoholic dimethylglyoxime is added, then a small excess of either ammonia or sodium acetate. The precipitate is filtered while hot on to a Gooch crucible, washed with hot water, and dried at 110°–120°. Its formula is $(CH_3 \cdot C:NO)_2Ni + (CH_3 \cdot C:NOH)_2$, and it contains 20·31 p.c. of nickel ; it has no definite melting-point, but sublimes at 250°. Ammonium salts do not interfere ; if the acetate method is employed, the original solution should be nearly neutralised with ammonia before

adding the oxime and acetate (Brunck, Zeitsch. angew. Chem. 1907, 20, 1844). As the precipitate of nickel glyoxime is very voluminous, it is advisable to work with solutions containing not more than about 0·1 gram nickel, owing to the difficulty of filtration, and again in order to avoid waste of material, the cobalt, if present, should not exceed 0·1 gram, otherwise a large excess of ammonium hydroxide and dimethylglyoxime is necessary in order to prevent its precipitation.

By either of the above methods, cobalt and zinc may be separated from nickel ; but about twice the theoretical amount of reagent is necessary. Manganese, of course, can only be separated by the acetate method. Iron, aluminium, and chromium may be separated by the ammonia method, if tartaric acid be previously added (and, in addition, ammonium chloride in the case of chromium). Iron may also be separated in acetic acid solution, provided it is in the ferrous state (Brunck, Zeitsch. angew. Chem. 1907, 20, 1845 ; Prettner, Chem. Zeit. 1909, 33, 396, 411 ; Ivanicki, Chem. Zeit. Rep. 1908, 32, 644 ; Rhead, Analyst, 1910, 35, 97 ; *v. also* ANALYSIS).

The oxime is sufficiently expensive to make its recovery desirable. This may be effected by dissolving the nickel derivative in aqueous potassium cyanide and acidifying with acetic acid. The precipitated dimethylglyoxime is purified by recrystallisation from hot alcohol, after decolourisation with charcoal (*v.* KETONES).

DIMETHYLMALONIC ACID *v.* GLUTARIC ACID.

DIMETHYLOXALIC ACID *v.* HYDROXYBUTYRIC ACIDS.

αα-**DIMETHYLPROPIONIC ACID** *v.* VALERIC ACID.

DIMETHYLPYRROLE *v.* BONE OIL.

DIMETHYLSAFRANINES *v.* AZINES.

DIMETHYLTRIAZINE, *Diazoaminomethane* *v.* DIAZO- COMPOUNDS.

DINAPHTHAZINES *v.* AZINES.

DINITROANTHRAQUINONES.

1 : 5-Dinitroanthraquinone (m.p. 330°)
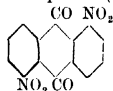
is made, together with the 1 : 8 isomeride, by adding sodium nitrate to anthraquinone dissolved in sulphuric acid. By extraction with alcohol or acetone the 1 : 8-dinitroanthraquine (m.p. 312°)
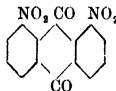
is removed.

Used in the manufacture of anthracene blues. *See* ALIZARIN AND ALLIED COLOURING MATTERS.

DINITROBENZENEDIAZO-OXIDE *v.* DIAZO-COMPOUNDS.

DINITROBENZENES *v.* BENZENE AND ITS HOMOLOGUES.

2 : 4-**DINITRO-4'-HYDROXYDIPHENYLAMINE**
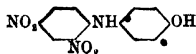
Made by boiling together in water containing chalk a mixture of 4-chloro-1 : 3 dinitrobenzene and *p*-aminophenol in molecular proportions ; m.p. 190°. Used in the manufacture of sulphide dyes (*q.v.*).

DINITRONAPHTHALENES *v.* NAPHTHALENE.

DINITROPHENOLS *v.* NITROPHENOLS AND THEIR HOMOLOGUES.

DINITROSTILBENEDISULPONHIC ACID

$$NO_2\!\!<\!\!\diagdown>\!\!CH:CH\!\!<\!\!\diagdown>\!\!NO_2$$
$$SO_3H \qquad SO_3H$$
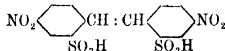
Obtained by warming a solution of sodium *p*-nitrotoluene sulphonate containing sodium hydroxide with sodium hypochlorite when sodium dinitrostilbenedisulphonate separates on cooling. The free acid is obtained by treating the sodium salt with hydrochloric acid. Pale yellow needles.

DINITROTOLUENES *v.* BENZENE AND ITS HOMOLOGUES, NITRATION OF.

DIOCTYLMALONIC ACID

$$(C_8H_{17})_2C(CO_2H)_2$$
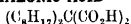
Prepared from diethylmalonic ester, sodium methoxide and octyl iodide, and subsequent decomposition of the ester thus formed with caustic potash (Conrad and Bischoff, Annalen, 204, 163) ; m.p. 75°.

DIOFORM. Trade name for *symm.* 1·2-*di*-
chlorethylene (acetylene dichloride) $\begin{Vmatrix} CHCl \\ CHCl \end{Vmatrix}$
(*q.v.*). Suggested as an anæsthetic.

DIOGEN. Trade name for sodium amino-naphthol-disulphonate.

DIOGENAL. Trade name for dibromo-propyl diethylbarbituric acid.

DIONINE. Ethyl morphine hydrochloride, *v.* OPIUM and SYNTHETIC DRUGS.

DIOPSIDE. A double salt meta-silicate of calcium and magnesium in which a part of the magnesium is usually replaced isomorphously by an equivalent amount of ferrous oxide, the formula being Ca(Mg,Fe)(SiO₃)₂. It is a member of the monoclinic series of the pyroxene group, and is of importance as a rock-forming mineral ; while occasionally, when transparent and of a rich bottle-green colour, it is employed as a gem-stone. The depth of colour, sp gr. (3·2–3·3), and other physical characters vary with the percentage of iron present, which in material of gem quality, such as the crystals from Ala in Piedmont, and the Zillerthal in the Tyrol, amounts to about 3–4 p.c. FeO. The hardness is 6.   L. J. S.

DIOPTASE. Hydrous silicate of copper, H_2CuSiO_4, crystallising in the rhombohedral system with parallel-faced hemihedrism. The water is expelled only at a red heat, and the formula has consequently been variously interpreted as an acid ortho-silicate, or as a basic meta-silicate. F. Zambonini (1908) concludes from dehydration experiments that the formula is $CuSiO_3 \cdot H_2O$, with the water held in solid solution in the meta-silicate. The mineral is of a characteristic emerald-green colour (hence the name emerald-copper ; Ger., Kupfer-Schmaragd), and transparent crystals have occasionally been cut as gem-stones. For this purpose, however, the hardness (H.=5) is rather low ; sp.gr. 3·3. The best crystals are found on the limestone hill of Altyn-Tübe in the Kirghiz Steppes, Siberia, and in the copper mines near Mindouli in the French Congo.

An allied mineral, *plancheite* (of A. Lacroix, 1908,=*shattuckite* of W. T. Schaller, 1915), occurs as blue, fibrous concretions associated with dioptase in the French Congo. This has the composition $2CuSiO_3 \cdot H_2O$, representing a partly dehydrated dioptase.   L. J. S.

DIORITE. An igneous rock composed essentially of plagioclase felspar (oligoclase to labradorite) and hornblende, and with a coarse- to medium-grained crystalline-granular texture. It belongs, with granite, to the series of plutonic rocks, and · is of intermediate composition (SiO_2, 52–60 p c.), falling between syenite and gabbro. Its volcanic equivalent is andesite. Other minerals may also be present as essential constituents of the rock, and accordingly the following varieties are distinguished : hornblende-diorite (diorite proper), augite-diorite, enstatite-diorite, mica-diorite (the mica here being biotite), quartz-mica-diorite, quartz-diorite (or tonalite). The colour is usually dark grey or greenish-black, and for this reason the rock is included under the general term 'greenstone.' The sp gr. ranges from 2 8 to 3·1 ; the porosity is low, 0·25 p.c. ; and the crushing strength 1640 to 1830 tons per square foot. Under I is given Brögger's average of sixteen analyses of typical diorites ; analysis II. is of diorite from Strathspey, Scotland ; III. of quartz-diorite from Spanish Peak, Plumas Co., California (including BaO 0 04, CO₂ 0 20, P_2O_5 0·25, SO_3 0·03) ; IV. hornblende-augite-diorite from Inchnadamph, Sutherlandshire (including CO_2 0 54).

	I.	II.	III.	IV.
SiO_2	56 52	53·22	59·68	52·47
TiO_2	0·25	—	0·65	—
Al_2O_3	16·31	16 84	17·09	12·15
Fe_2O_3	4·28	—	2·85	3·47
FeO	5 92	9·27	2·75	5·23
CaO	6·94	8 53	6·62	9·71
MgO	4·32	6·48	3·54	9·94
K_2O	1·44	1·39	1·81	2·26
Na_2O	3 43	3·54	3 87	2·81
H_2O	1·03	0·95	1·15	1·62
	100·34	100·22	100·03	100·20

Diorites are of wide distribution and are very common in association with granitic rocks in the southern uplands and highlands of Scotland. They are extensively quarried for road-metal and paving-setts in the Channel Islands, Guernsey, Jersey, and Alderney, and at Brazil Wood near Mount Sorrel in Leicestershire. Owing to the difficulty of working the rock and its dull colour, it is not much used as a building stone, except locally. Certain coarse-grained varieties are, however, polished for ornamental purposes. For example, a variety from Corsica, known as napoleonite, corsite, or ball-diorite, shows a spheroidal structure with alternating concentric layers of light felspar and dark hornblende.   L. J. S.

DIOSCORINE $C_{13}H_{19}O_2N$, greenish-yellow plates, m.p. 43·5°, occurs in *Dioscorea hirsuta* (Blume) tubers of Japan. Bitter and poisonous (Gorter, Rec. trav. chim. 1911, 30, 161). Has an action like picrotoxin.

DIOSPHENOL, *Buchu camphor v.* BUCHU.

DIOXINE. Gambine H. 1-nitroso-2 : 7-dihydroxynaphthalene, *v.* QUINONEOXIME DYES.

DIOXOREA. A genus of plants of the Dioxoreaceous order, the tubers of which are known as yams, and are largely eaten in the West Indies and other tropical countries. *D. batatas* (Decne.) is the plant producing tubers known as 'sweet-potatoes,' which are cooked and eaten as a substitute for potatoes.

DIOXYGEN. Trade name for a 3 p.c. solution of hydrogen peroxide.

DIPHENAL, *Diaminohydroxydiphenol,* used as a photographic developer.

DIPHENAZINE *v.* AZINES.

o-**DIPHENETIDINE** *v.* DIPHENYL.

DIPHENYL. This hydrocarbon, which has the molecular formula $C_{12}H_{10}$, is structurally composed of two benzene nuclei joined together by a bond linking two carbon atoms, one in each ring. The carbon atoms are numbered for the purposes of nomenclature in the following way :—
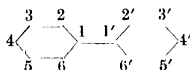
Although of minor importance, diphenyl is nevertheless the parent substance of a large number of important bases which have found application in the preparation of the so-called substantive cotton dyes, that is to say, of colouring matters which will affix themselves to the vegetable fibres without the aid of a mordant. These bases are, however, not derived directly from the hydrocarbon, but are prepared by an indirect method which will be described later.

Diphenyl was originally obtained by Fittig (Annalen, 121, 363) from an ethereal solution of bromobenzene by the action of metallic sodium

$$C_6H_5Br + BrC_6H_5 + 2Na \rightarrow C_6H_5-C_6H_5 + 2NaBr$$

but it is more conveniently prepared by the method discovered by Berthelot (Ann. Chim. Phys. [4] 9, 453 ; [4] 12, 185), who obtained it by passing the vapour of benzene through a red-hot tube

$$C_6H_5H + HC_6H_5 \rightarrow C_6H_5-C_6H_5 + H_2$$

The following procedure is recommended (Schultz, Ber. 9, 547 ; Hubner, Annalen, 209, 339 ; Smith and Lewcock, Chem. Soc. Trans. 1912, 101, 1453 ; [apparatus] La Coste and Sorger, (Annalen 230, 5). The vapour from a quantity of benzene (free from thiophen), contained in a large flask heated on the water-bath, or produced by dropping the liquid into a copper flask heated to 150°, is allowed to pass through an iron tube, filled with pumice, which is heated to about 720° in a combustion furnace ; the lower end of the iron tube is attached to a condenser and receiver, in which the products are collected. When all the benzene has distilled over, the distillate is again placed in the flask, and the vapour passed anew through the red-hot tube, or the process may be made continuous. The ultimate product is then fractionally distilled, and the portion boiling between 250° and 260°, which solidifies on cooling, is purified by recrystallisation from alcohol. The yield is about 50–60 p.c. The pyrogenic preparation can also be effected by means of an incandescent filament of carbon, platinum, or nickel (Löb, Zeitsch. Elektrochem. 1902, 8, 777). Diphenyl separates from alcohol as large, lustrous laminæ which melt at 70·5°. It boils at 254° (corr.), and is insoluble in water. The

hydrocarbon, when oxidised by chromic acid passes into benzoic acid.

Bennett and Turner (Chem. Soc. Trans. 1914, 105, 1057) found that chromic chloride reacted quantitatively with magnesium phenyl bromide to form diphenyl. Krizewsky and Turner (Chem. Soc. Trans. 1919, 115, 559) have observed that anhydrous cupric chloride behaves similarly, yields of about 85 p.c. of the theoretical amount of diphenyl being thus obtained.

Derivatives of Diphenyl and their Orientation.—The more important derivatives of diphenyl are not prepared directly from the hydrocarbon, but from certain nitro- derivatives of benzene in a manner to be described later. The hydrocarbon yields, however, halogen, nitro- and sulphonic acid derivatives analogous to those prepared from benzene, substitution taking place in either one or both rings according to the conditions of the experiment. The method of orientation adopted for these compounds may be briefly described as follows (Schultz, Annalen, 174, 201 ; Schmidt and Schultz, *ibid.* 207, 320). When diphenyl is treated with bromine, it yields a monobromodiphenyl, a substance which, on oxidation, is converted into *p*-bromobenzoic acid, thus :
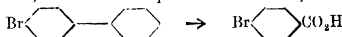
It follows, therefore, that in bromodiphenyl the bromine atom must have entered the *para*-position with respect to the linking carbon atom. When bromodiphenyl is treated with nitric acid, it is converted into a monobromo-mononitrodiphenyl, a substance which, on oxidation, yields a mixture of *p*-bromobenzoic acid and *p*-nitrobenzoic acid. It is therefore apparent that the formula of this bromonitro-derivative must be :
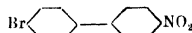
The same compound is also obtained from dinitrodiphenyl (m.p. 198°) and then replacing the amino- group by bromine by means of the diazo- reaction. Hence dinitrodiphenyl and its reduction product are di-*para*- derivatives. Since, however, nitroaminodiphenyl, on reduction, furnishes the diamino- derivative, benzidine, the latter is also a di-*para*- compound, or 4 : 4'-diaminodiphenyl, the preparation of which is described later.

The transformation of the simplest aromatic hydrocarbon benzene into diphenyl by the action of heat has already been mentioned. This transformation can, however, be effected much more readily by the oxidation of certain derivatives of benzene, and especially those which, like the phenols, have a reactive hydrogen in the *para*- position with respect to the substituting group. Thus phenol itself and also resorcin readily pass into derivatives of diphenyl when fused with potash (Barth, Annalen, 156, 95). With hydroquinone, the transformation is still more readily effected and the action of the mildest oxidising agents is sufficient for the purpose (Nietzki and Bernard, Ber. 31, 1334).

The primary bases of the benzene series, such as aniline, do not lend themselves to the production of derivatives of diphenyl, but the tertiary bases readily do so ; thus dimethylaniline yields tetramethylbenzidine when oxidised (Michler and Pattinson, Ber. 14, 2162 and 2164)

It has also been found that certain azo-derivatives of benzene can be transformed by oxidation into tetrazo- derivatives of diphenyl, and in this way Congo red can be formed by treating benzeneazonaphthionic acid with manganese dioxide and sulphuric acid :

$$C_6H_5N=N—C_{10}H_5(NH_2)SO_3H$$
$$+O$$
$$C_6H_5N=N—C_{10}H_5(NH_2)SO_3H$$
$$\rightarrow \begin{vmatrix} C_6H_4—N=N—C_{10}H_5(NH_2)SO_3H \\ C_6H_4—N=N—C_{10}H_5(NH_2)SO_3H \end{vmatrix} +H_2O$$
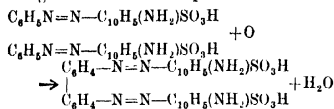
Derivatives of diphenyl can also be prepared from certain diazonium salts of the benzene series. Thus Kuhling has shown (Ber. 28, 41 ; 29, 165) that when an isodiazo- salt is treated with an aromatic hydrocarbon in the presence of an acid chloride, the following reaction ensues :—

$$NO_2·C_6H_4N_2OK +C_6H_6+CH_3COCl$$
$$\rightarrow NO_2C_6H_4—C_6H_5+N_2+ KCl+CH_3CO_2H$$
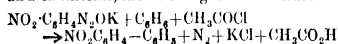
This reaction has been simplified by Bamberger (Ber. 28, 403 ; 29, 272 and 465), who uses free isodiazobenzene hydroxide, and shows that it passes, in the presence of benzene, without any condensing agent, into a derivative of diphenyl. Many derivatives of diphenyl can also be formed by the method of Ullmann, in which halogen derivatives of benzene are treated with finely divided copper (Ber. 43, 2682 ; Annalen, 1904, 332, 38).

Benzidine and the 'Benzidine Rearrangement.'—The benzidine rearrangement, which has been widely applied to the preparation of a large number of important bases used in the production of the substantive cotton dyes, is the name given to the change which an aromatic hydrazo- compound undergoes when treated with acids or certain acid reagents. The change is effected by the wandering of the hydrogen atom which is in the para- position in each ring on to the nitrogen atom attached to that ring ; at the same time, the link between the nitrogen atoms is broken, and the two aromatic nuclei are joined together. It is apparent, therefore, that only those hydrazo- derivatives of benzene which have their para- position free will undergo this transformation.

Hydrazobenzene. Benzidine.
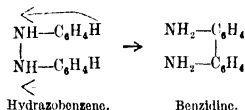
The history of the discovery of this rearrangement is briefly as follows : Zinin (J. pr. Chem. 36, 93), in the first instance, showed that azobenzene $C_6H_5—N=N—C_6H_5$, when treated with alcoholic ammonium sulphide, passed into a crystalline compound which, when dissolved in alcohol and boiled with sulphuric acid, gave the sparingly soluble sulphate of a base This base he called benzidine.

It soon became apparent that the substance responsible for the formation of benzidine must be an intermediate product formed by the action of the reducing agent on azobenzene. This view was confirmed experimentally by A. W. Hofmann (Jahresbericht, 1863, 424), who prepared the intermediate product, hydrazobenzene, and found that it passed with remarkable ease into benzidine when treated with mineral acids.

Finally, Fittig (Annalen, 124, 280) showed that benzidine was identical with the base formed by the reduction of 4-4'-dinitrodiphenyl, and hence established the constitution of the base as 4-4'-diaminodiphenyl.

Manufacture of Benzidine.—A jacketed iron pan fitted with an agitator, reflux condenser, &c., is charged with 100 kilos. of nitrobenzene and 50 kilos. of alcohol. This mixture is heated to boiling, and 150–160 kilos. of zinc dust are added. The stirring must be very efficient during the next operation, which requires 5–6 hours, of adding gradually a mixture of 100 kilos. of alcohol and 40 kilos. of sodium hydroxide solution (36°–40°B.). The reaction is vigorous and is regulated by the rate of addition of the alkali and, if necessary, by cooling. When all the alkali has been added the mixture is stirred until it is of a uniformly grey colour, and to obtain this more zinc may have to be introduced. The alcohol is then distilled off by means of steam, and the residue is thrown on a fine sieve which retains the hydrazobenzene and allows the zinc dust, zinc oxide, &c., to pass through. Another method of working up consists in diluting the reduction mixture with water, carefully neutralising with hydrochloric acid, and filtering off the hydrazobenzene.

The latter is transformed into benzidine by mixing it with ice and acidifying with concentrated hydrochloric acid. After some time water is added and steam introduced so as to dissolve the benzidine hydrochloride, the solution is filtered, and the benzidine sulphate precipitated by adding sodium sulphate solution. This is filtered off, washed, and the base obtained by boiling with sodium hydroxide solution, cooling, collecting, and distilling in a vacuum still. The yield is about 80 p.c. of the theoretical.

The above process can also be carried out without the use of alcohol, or solvent naphtha can be employed instead.

The electrolytic reduction of nitrobenzene to hydrazobenzene is the subject of a number of patents, but it would not appear that this method is yet applied on the large scale (cf. Löb, Ber. 1900, 33, 2329).

The production of benzidine from azobenzene is easily effected by an electrolytic method with titanium salts or vanadium trioxide used as catalysts. The azobenzene is suspended in 30 p.c. sulphuric acid containing 10 p.c. titanous sulphate ; a lead cathode is used with a current of 3–4 amp. per square dcm. at 3–4 volts (D.'R. PP. 168273 and 172654).

The presence of small quantities of hydriodic acid facilitates the reduction of azobenzene to benzidine by means of sulphurous acid (D. R. P. 172569).

Benzidine, when pure, forms colourless lustrous laminæ, which melt at 127·5°–128° ; it boils at 400°–401° (740 mm.). The base is characterised as a para- derivative by the formation of quinone when it is oxidised by manganese dioxide and sulphuric acid. It can be identified by a number of colour reactions : chlorine, bromine, potassium permanganate, potassium ferricyanide, and chromic acid, producing characteristic shades. The most characteristic salts of benzidine are the sulphate $C_{12}H_{12}N_2,H_2SO_4$, and the chromate $C_{12}H_{12}N_2,H_2CrO_4$. Both salts are sparingly soluble in alcohol and in water.

When treated with nitrous acid, benzidine hydrochloride is transformed into a tetrazonium salt of diphenyl

$$C_6H_4N_2Cl$$
$$|$$
$$C_6H_4N_2Cl$$

which reacts readily with the usual second components of the azo- colouring matters, forming azo- compounds, the solutions of which possess the property of dyeing the vegetable fibres without the aid of a mordant. The number of colouring matters of this kind prepared from benzidine is largely increased owing to the insoluble character of the diazonium salt

$$C_6H_4N_2X$$
$$|$$
$$C_6H_4N_2Cl$$

in which one molecule of a second component, XH, has combined with the tetrazonium salt derived from benzidine. These diazonium salts, when combined with some other second component, YH, yield mixed azo- colouring matters of the formula

$$C_6H_4N_2X$$
$$|$$
$$C_6H_4N_2Y$$

Benzidine in the presence of hydrogen peroxide is used as a test for blood, with which it gives a blue colouration. The test solution is made by taking 10 drops of a concentrated solution of benzidine in glacial acetic acid, and adding 2 c.c. of a 3 p.c solution of H_2O_2. Sensitiveness—1 part in 200,000. (Utz, Chem. Zeit. **1907**, 31, 737; Schumm, Pharm. Zeit. 1907, 52, 604; McWeeney, Sci Proc. Roy. Dubl. Soc. 1909, 12, 216; Bordas, Compt. rend. 1910, 150, 562; Gigli, Boll. chim. farm. 1910, 49, 955; *cf.* O. and R. Adler, Zeitsch. physiol. Chem. 1904, 41, 59.)

Homologues and Derivatives of Benzidine used in the Preparation of the Substantive Cotton Dyes. —Although a great many of the derivatives of benzidine yield azo- colouring matters which are substantive to the vegetable fibres, yet this property is largely dependent on the position of the groups substituting the hydrogen atoms of the diphenyl molecule. Thus it has been found that when the substituting groups are in the meta- position to the coupling bond, as in

o-Tolidine.

o-Dianisidine.
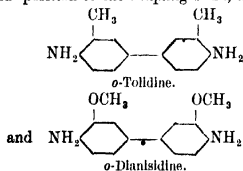
the azo- colours formed are substantive to cotton. If, however, groups are in the ortho-position, as in

Benzidine-*m*-disulphonic acid.

Diaminodiphenic acid.
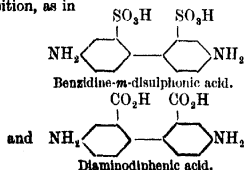
the property of the azo- colours of dyeing unmordanted vegetable fibre is lost. The ortho-derivatives nevertheless yield substantive cotton dyes if ring formation takes place between the substituting groups in those positions ; thus :

Diaminocarbazole.

Benzidine sulphone.
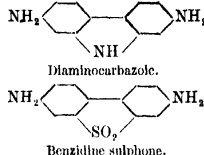
yield azo- dyes substantive to cotton.

Benzidine-o-disulphonic acid is prepared by heating benzidine sulphate with 2 parts of sulphuric acid for 36-48 hours at 210° (Ber. 1889, 22, 2464 ; Eng. Pat. 1074, 1884 ; D. R. P. 27954).

o-*Dichlorobenzidine* is prepared from *o*-chloronitrobenzene, and is also produced by chlorinating diacetylbenzidine (Eng. Pat. 25725, 1896 ; Fr. Pat. 265155 ; D. R. P. 94410 ; U.S. Pat. 625174).' It melts at 133°.

m-*Nitrobenzidine*, obtained by treating a solution of benzidine in sulphuric acid with one equivalent of nitric acid or potassium nitrate (Tauber, Ber. 1890, 23, 796 ; Eng. Pat. 13475, 1892 ; Fr. Pat. 223176 ; D R. P. 72867 ; U.S. Pat. 493583), melts at 143° ; when two equivalents of the nitrating agent are used, m-*dinitrobenzidine*, m.p 214°, is produced. Mononitration of diacetylbenzidine or phthalylbenzidine, and subsequent hydrolysis of the product, furnishes o-*nitrobenzidine*, m p. 190° (Koller, Ber. 1904, 37, 2883 ; Fr. Pat. 203468), whilst two different o-*dinitrobenzidines*, m.p. 275° and 233°, are obtained by the dinitration of diacetylbenzidine and diphthalylbenzidine respectively (Trans. Chem. Soc. 1912, 101, 2298).

The following compounds, prepared from the corresponding nitro- derivatives of benzene, are of importance :—

o-*Toluidine*, 4 - 4' - diamino - 3 - 3' - dimethyl diphenyl $NH_2 \cdot C_6H_3(CH_3)-C_6H_3(CH_3)NH_2$ from o-nitrotoluene, forms glistening plates, melting at 129°. It is sparingly soluble in water, but readily soluble in alcohol and in ether. The sulphate is sparingly soluble in water.

o-*Dianisidine*, 4-4'-diamino-3-3'-dimethoxy-diphenyl $NH_2 \cdot C_6H_3(OCH_3)-C_6H_3(OCH_3)NH_2$, from o-nitroanisole, forms colourless leaflets, melting at 135°. (For its manufacture, *see* Jansen, Zeitsch. Farb. Ind. 1913, 12, 247.)

o-*Diphenetidine*, 4-4'-diamino-3-3'-diethoxy-diphenyl $NH_2 \cdot C_6H_3(OC_2H_5)-C_6H_3(OC_2H_5)NH_2$, from o-nitrophenetole, forms needles or leaflets melting at 117°.   J. F. T.

DIPHENYLAMINE was first obtained by Hofmann, in 1864, by distilling aniline blue (Annalen, 132, 163), and in small quantity by distilling rosaniline and leucaniline. De Laire, Girard, and Chapoteaut discovered an easier method of preparing it by heating aniline with the hydrochloride at 210°–240° (Zeitsch. Chem. 1866, 438 ; Compt. rend. 63, 91)

$$C_6H_5NH_2 + C_6H_5NH_2HCl = NH(C_6H_5)_2 + NH_4Cl$$

This reaction is greatly facilitated by the use of certain catalysts. It may also be obtained by heating phenol with the double compound of

aniline and zinc chloride at 250°–260° (Merz and Weith, Ber. 13, 1298, 1880) :

$$C_6H_5NH_2+C_6H_5OH=(C_6H_5)_2NH+H_2O$$
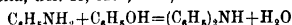
and by heating aniline and diazoaminobenzene to 150° till the evolution of nitrogen ceases. In this last reaction, ortho- and para- aminodiphenyl are formed at the same time (Hirsch, D. R. P. 62309). Diphenylamine has also been prepared by the action of aniline on bromobenzene in presence of cuprous iodide (Goldberg, D. R. P. 187870, 1906). Aniline, when heated with ferric chloride, finely divided copper, and iodine, is converted into diphenylamine. Other catalysts can also be used (Rogers and de Nemours, U S. Pat. 1314538).

Manufacture —Aniline (1 mol.) is heated with aniline hydrochloride (1 mol.) for 30–35 hours in an autoclave at 220°–230°. The product is extracted with hot dilute hydrochloric acid which dissolves the aniline hydrochloride and converts the diphenylamine into the free base, forming an oil which solidifies on cooling. The cake of diphenylamine is washed and then distilled alone or in a current of steam. Yield, 60–70 p.c. of the aniline employed. It is used in the manufacture of diphenylamine blue, diphenylamine orange, and aurantia (*v. infra*).

Properties —Monoclinic laminæ ; m.p. 54° ; b.p. 310° ; almost insoluble in water, soluble in alcohol, benzene, and ether. It is feebly basic, and the salts are hydrolysed by an excess of water.

Reactions.—The hydrogen of the imino- group is replaceable by alkyl or acyl radicals (Bösekon, Rec trav. chim. 1912, 31, 350). With methyl iodide it gives a methyl derivative ; with benzyl chloride, a benzyl derivative With formic or oxalic acid it yields formyldiphenylamine, m.p. 74° ; with acetic acid or the acid chloride, an acetyl derivative, m p. 103° ; and with benzoyl chloride, a benzoyl derivative, m.p. 180°. When heated with zinc chloride, the acyl derivatives lose water and form acridine derivatives. Formyldiphenylamine gives acridine

$$C_6H_5\diagdown \overset{N}{\underset{CHO}{|}} \diagup C_6H_5 = C_6H_4 \diagdown \overset{N}{\underset{CH}{|}} \diagup C_6H_4 + H_4O$$
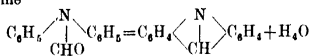
The acetyl compound yields methylacridine (Bernthsen and Bender, Ber. 1883, 16, 767). Diphenylamine also gives acridine by heating with chloroform and zinc chloride or aluminium chloride

$$(C_6H_5)_2NH + CHCl_3 = C_6H_4 \diagdown \overset{N}{\underset{CH}{|}} \diagup C_6H_4 + 3HCl$$
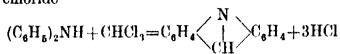
(O. Fischer and Körner, Ber. 1886, 17, 101). With excess of oxalic acid, diphenylamine is converted into diphenylamine blue

$$3(C_6H_5)_2NH + CO_2 = C\diagdown \overset{C_6H_4 \cdot NH \cdot C_6H_5}{\underset{C_6H_4\!-\!N C_6H_5}{\overset{|}{\underset{}{\diagup}}} C_6H_4 \cdot NH \cdot C_6H_5} + 2H_2O$$
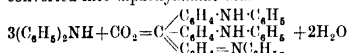
Carbon tetrachloride reacts like oxalic acid, and gives the same blue colour. With sulphur, thiodiphenylamine, the parent substance of methylene blue, is produced :

$$(C_6H_5)_2NH + 2S = C_6H_4 \diagdown \overset{NH}{\underset{S}{}} \diagup C_6H_4 + H_2S$$
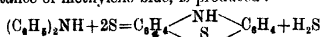
(Bernthsen, Ber. 1883, 16, 2897). When the vapour of diphenylamine is passed through a red-hot tube, carbazole is formed :

$$C(C_6H_5)_2NH = \overset{C_6H_4}{\underset{C_6H_4}{|}} \diagup NH + H_2$$
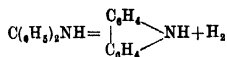
(Graebe, Annalen, 167, 127) ; and the latter is also obtained from thiodiphenylamine and copper powder (Goske, Ber. 1887, 20, 233).

Tests.—A solution of diphenylamine in conc. sulphuric acid gives a deep indigo-blue colour with nitric, nitrous or chloric acid (Ber. 1912, 45, 2641 ; 1913, 46, 2286 ; Chem. Zeit. 1912, 26, 1239 ; Bull Soc. Chim 1914, (14), 15, 186. The commercial product is a pale-yellow solid, melting not much below 54° ; it should contain no oil, possess no unpleasant odour, nor turn brown on exposure to air.

Derivatives.—By passing chlorine into a solution of diphenylamine in acetic acid, a tetrachlorodiphenylamine is formed. 4- chloro-2·6 dinitrodiphenylamine has been prepared (Ullmann and Shrirang, Ber. 1911, 44, 3730. Bromine in alcoholic solution produces a tetrabromodiphenylamine ; in acetic acid, a hexabromo- derivative ; and at a high temperature in presence of iodine, an octo- and deca-bromo-compound. Diiododiphenylamine is formed by the action of iodine in alcoholic solution in presence of mercuric oxide. Bromine derivatives of nitrodiphenylamine are also known (H. and P. Ryan, Proc. Roy Irish Acad 1919, 34, 218). By nitration in acetic acid solution, a tetranitro- derivative is formed, whilst direct nitration yields a hexanitro- compound, crystallising in yellow prisms, and melting at 238°. The latter has strongly acid characters, and gives an ammonium salt which is used as a yellow dye known as *aurantia* (q v.). Nitrosodiphenylamine is obtained by acting upon the base with amyl nitrite.

Alkyl Derivatives —Methyldiphenylamine is obtained by heating together diphenylamine (100 parts) conc. hydrochloric acid (68 parts), and methyl-alcohol (24 parts) for 10 hours to 250° in an autoclave (Girard, Bull. Soc. chim. [ii.] 23, 2). It is a liquid ; b.p. 282°. The ethyl derivative is obtained in a similar way ; b.p. 293°. The amyl derivative boils at 330°–340°. Benzyl chloride produces a benzyl derivative which is used in the preparation of viridine and alkali green.

Amino- Derivatives.—2-Chloro-5-nitrobenzenesulphonic acid combines with *p*-phenylenediamine to form 4-nitro-4-aminodiphenylamine sulphonic acid

$$NO_2\diagup\!\!\diagdown\!\!-NH-\diagup\!\!\diagdown\!\!\overset{SO_3H}{}NH_2$$
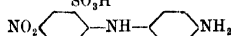
which, on reduction, gives *p*-diaminodiphenylamine sulphonic acid (Baeyer & Co., D. R. P. 86250, 1894 ; Farb. vorm. Meister, Lucius and Brüning, D. R. P. 265197, 1914). Similar derivatives are obtained by the action of *p*-aminophenol, aminophenol sulphonic acid, and *p*-aminosalicylic acid. The sulphonic acid group may be removed by heating with dilute acids under pressure (Meister, Lucius, and Brüning, D. R. P. 112180, 1899). Paraphenylenediamine and phenol in presence of copper salts and a solution of hypochlorite are oxidised to *p*-amino-*p*-hydroxydiphenylamine (Aktien Gesell. D. R. P. 204596, 1907). Aminohydroxydiphenylamine is also obtained by the electrolytic reduction of *m*-nitrodiphenylamine (Piccard and Lassen, J. Amer. Chem. Soc. 1918, 40, 1079). Diphenylamine derivatives prepared by the action,

of primary aromatic bases such as *p*-phenylene-diamine, *p*-aminophenol, and aminosalicylic acid on (1.3.4)-dinitrochlorobenzene, (1.3.4.6)-dinitrodichlorobenzene, and (1.4.3)-nitrochlorobenzene sulphonic acid, are used in the preparation of sulphide colours, of which the most important is dinitroxydiphenylamine

$$C_6H_3(NO_2)_2NH \cdot C_6H_4(OH)$$
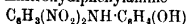
obtained from *p*-aminophenol and dinitrochlorobenzene. Phenoxydinitrodiphenylamine is obtained from 1 3 dichloro 4·6 dinitrobenzene, potassium phenate and aniline (Borsche, Ber. 1917, 50, 1339).

Diphenylaminedicarboxylic acid is obtained by the action of anthranilic acid on *o*-chlorobenzoic acid in presence of finely divided copper. Other amino-acids behave similarly (Meister, Lucius, and Brüning, D. R P. 148179, 1902; Purgotti, Gazetta, 1914, 44, i, 386)

Diphenylamine combines with formaldehyde, and the product forms an additive compound with sodium bisulphite

$[(C_6H_5)_2N]_2 + HSO_3Na$
$\quad = (C_6H_5)_2N \cdot CH_2 \cdot SO_3Na + (C_6H_5)_2NH$
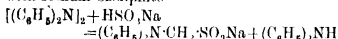
(Bad. Anilin-Sod. Fab. D. R P 158718, 1904) For nitro- derivatives, *see* Borsche and Rantschelf, Annalen, 1911, 379, 152; B Linke, J. prakt. Chem. 1915, ii, 91, 202; Eckert and Steiner, Monatsh 1914, 35, 1453; Meldola, Foster and Brightman, Trans 1917, 111, 546; Ryan and Glover, Proc. Roy. Irish Acad. 1918, 34, [B] 97, 194; J. Soc. Chem. Ind. 1918, 762, A; van Duin and van Lennep, Rec. trav. chim. 1919, 38, 358; Hofman and Dame, J. Amer. Chem. Soc. 1919, 41, 1413. J B. C.

DIPHENYLAMINE BLUE *v.* TRIPHENYL-METHANE COLOURING MATTERS.

DIPHENYLAMINE ORANGE *v.* AZO- COLOURING MATTERS.

DIPHENYLBISDIAZONIUM CHLORIDE *v.* DIAZO- COMPOUNDS.

DIPHENYL BROWN, -CATECHINE, -CHRYSOIENES, -CITRONINE, -FAST BLACK, -FAST YELLOW, -GREEN, -ORANGE, -RED *v.* AZO-COLOURING MATTERS.

DIPHENYL-DIMETHYLOLID
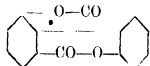
The dilactone of dihydroxy-diphenyl dicarboxylic acid, is the mother substance of a small series of colouring matters, of which but one natural representative, ellagic acid, is as yet known to exist. The methylolid grouping —CO—O— present in the compounds has a feebler chromophoric character than the carbonyl itself, and on this account the dyeing properties of the members of this class are inferior as regards strength to those of the benzophenone, flavone, and allied dyestuffs. That the diphenyl linkage here exerts an influence is certain, for gallotannin containing as it does digalloyl nuclei :

$(OH)_3C_6H_2$—CO—O—$C_6H_2(OH)_2$—CO—O—

dyes only with iron and titanium mordants, and again such an effect is clearly seen by a comparison of benzophenone and fluorenone :
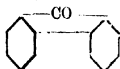
for whereas the former is colourless, the latter possesses a strong yellow tint.

Though diphenyl-dimethylol is at present unknown, diphenyl-methylolid :
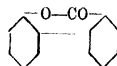
needles, melting at 92·5°, has been prepared by various methods, and of these that of Richter (J. pr. Chem. [2] 28, 294), who obtained it by the action of phosphorus oxychloride on ethyl salicylate :
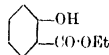
is the simplest.

Colouring matters derived from diphenyl-methylolid itself do not appear to exist in nature, though certain of them can be readily prepared by the action of alkali on diphenyl dimethylolid compounds, in which case hydrolysis followed by the elimination of a carboxyl group occurs :
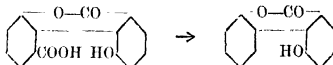
By a more drastic action of the alkali, hydroxy-diphenyl derivatives are produced :
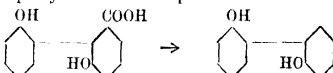
Interesting is the fact pointed out by Graebe (Ber. 1903, 36, 214) that by distillation with zinc-dust diphenylmethylolid yields fluorene :
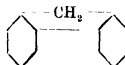
in addition to diphenyl and methyldiphenyl. Formerly the production of the first-named hydrocarbon from ellagic acid proved a stumbling-block in attempts to obtain a clear conception of its constitution. A. G. P.

DIPHENYLENEMETHANE *v.* FLUORENE.

DIPHENYLHYDRAZINE *v.* HYDRAZINES.

DIPHENYLHYDRAZONES *v.* HYDRAZONES.

DIPHENYLKETONE *v.* BENZOPHENONE and KETONES.

DIPHENYLMETHANE was first obtained by Jena, in 1870 (Annalen, 155, 86), by the dry distillation of barium diphenylacetate

$$[(C_6H_5)_2CH \cdot COO]_2Ba$$
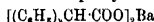
According to Zincke (Annalen, 159, 374), it is produced by the action of finely divided copper, iron, or zinc or their chlorides, on a mixture of benzyl chloride and benzene or by heating benzoylbenzoic acid with soda-lime. Friedel and Crafts (Bull. Soc. chim. [ii.] 41, 324) and Schwartz (Ber. 1881, 14, 1526) obtained it by the action of benzene on methylene chloride in presence of aluminium chloride ; E. & O. Fischer (Annalen, 194, 253), as by-product in the formation of triphenylmethane from chloroform and benzene in presence of aluminium chloride ; the Friedel-Crafts reaction applied to aromatic

alcohols in presence of benzene (Huston and Friedemann, J. Amer. Chem. Soc. 1916, 38, 25); and Hirst and Cohen (Chem. Soc. Trans. 1895, 67, 826), by the action of the aluminium-mercury couple on a mixture of benzyl chloride and benzene. It is also formed by the reduction of benzophenone (Zincke, Thörner, Ber. 1877, 10, 1473; Staedel, Annalen, 194, 307; Graebe, Ber. 1874, 7, 1624), and by the action of phosphorus pentoxide on benzyl ethyl ether (v. Meyer, J. prakt. chem. 1910, ii. 82, 538). But the methods which have found a technical application in the production of diphenylmethane derivatives, as well as of the parent hydrocarbon, are those of (1) Meyer and Würster, which consists in heating a mixture of benzyl alcohol, benzene and conc. sulphuric acid (Ber. 1873, 6, 693), and of (2) Baeyer, in which benzene, formaldehyde, or methylal are shaken together in presence of conc. sulphuric acid (Ber. 1873, 6, 221).

$$CH_2O + 2C_6H_6 = CH_2(C_6H_6)_2 + H_2O$$
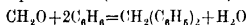
Properties.—Diphenylmethane crystallises in long, colourless, prismatic needles, possesses a fragrant smell, melts at 26°-27°, and distils without decomposition at 261°-262°. It dissolves easily in alcohol, ether, and chloroform.

Reactions.—On oxidation with chromic acid, it yields benzophenone. On passing the vapour through a red-hot tube, it is converted into o-diphenylenemethane. On heating it with sulphur to 250°, it gives tetraphenylethylene, and on prolonged chlorination with iodine chloride at 350° it breaks up into hexachlorobenzene and carbon tetrachloride (Ruoff, Ber. 1876, 9, 1485).

Nitro- Derivatives.—On nitration, diphenylmethane yields two dinitro- derivatives, one of which melts at 183°, and the second, which is the chief product, at 118°. Other dinitro- derivatives are obtained from nitrobenzyl chloride, benzene and aluminium chloride, nitrobenzyl alcohol, benzene and sulphuric acid or nitrobenzene, formaldehyde and sulphuric acid, in a similar manner to the parent hydrocarbon. Also nitrohydroxy- derivatives can be prepared by condensing nitrophenols and their ethers with formaldehyde and conc. sulphuric acid (D. R. P. 72490). The prolonged action of nitric and sulphuric acids gives rise to a tetranitro- derivative.

Amino- Derivatives.—The only substances possessing at the present time an industrial value are the amino- derivatives of diphenylmethane. They may be obtained by the reduction of the nitro- derivatives by tin and hydrochloric acid; but the more common method is to effect condensation between the aromatic base and formaldehyde, a general process for which a number of patents have been granted in recent years. Thus, by heating aniline, aniline hydrochloride and formaldehyde, 40 p.c., to 100°, 4,4'-diaminodiphenylmethane is produced (D. R. PP. 53937 and 55565). The reaction appears to occur in two stages, for on heating aniline, formaldehyde, and a strong alcoholic solution of potassium hydroxide, the following change takes place :—

$$CH_2O + 2C_6H_5NH_2 = C_6H_5NH\cdot CH_2\cdot NH\cdot C_6H_5 + H_2O$$
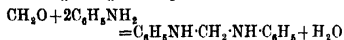
and the latter when heated with aniline and its hydrochloride passes into the diphenylmethane

derivative. A tetramethyldiamino- compound is obtained in a similar manner from dimethylaniline and formaldehyde in acid solution. Similarly, a diphenyldiamino- derivative

$$C_6H_5NH\ C_6H_4\cdot CH_2\cdot C_6H_4NH\cdot C_6H_5$$

has been prepared from diphenylamine and formaldehyde (D. R. P. 58072), a tetramethyldiaminodihydroxy- derivative

$$(CH_3)_2N(OH)C_6H_3\cdot CH_2\cdot C_6H_3(OH)N(CH_3)_2$$
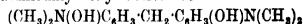
from dimethyl-m-amino phenol (D. R. PP. 63081 and 67001), and a diethoxydiaminodiphenylmethane $NH_2(C_2H_5O)C_6H_3\cdot CH_2\cdot C_6H_3(OC_2H_5)NH_2$ from o-phenetidine and formaldehyde in presence of hydrochloric acid (D. R. PP. 70402, 72490, 73951, 73946).

Other methods for obtaining 4,4'-diaminodiphenylmethane are (1) the action of p-aminobenzyl alcohol on aniline hydrochloride in aqueous solution (D. R. P. 96762), and (2) heating p-aminobenzylaniline with hydrochloric acid (D. R. P. 107718)

$$NH_2C_6H_4\cdot CH_2\cdot NHC_6H_5$$
$$= NH_2C_6H_4\cdot CH_2\cdot C_6H_4NH_2$$
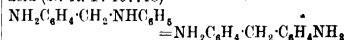
The 4·4 diaminodiphenylmethane has been prepared from p-aminobenzylaniline by heating with aniline and similar aromatic bases

$$NH_2C_6H_4\cdot CH_2NH\cdot C_6H_5 + C_6H_5NH_2$$
$$= NH_2\cdot C_6H_4\cdot CH_2\ C_6H_4\cdot NH_2 + C_6H_5NH_2$$
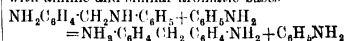
(v. Braun and Kruber, Ber. 1913, 46, 3952).

For diaminoditolylmethane see Farb. vorm. Meister, Lucius and Brüning, D. R. P. 252916, 1913.

A 1 1' dichloro 2.2' diamino diphenylmethane is described by Duval, Compt. rend. 1912, 154, 780, and by Meyer, Ber. 1914, 47, 1161, who prepared it from formaldehyde and o-chloraniline.

A tetrahydroxy- derivative was obtained by Ghosh and Watson (Chem. Soc. Trans. 1917, 111, 824) from quinol and formaldehyde.

Aryl derivatives of diphenylmethane, prepared by the Grignard reaction, are described by Boudroux, Compt. rend. 1915, 161, 131.

Sulphonic acids of diphenylmethane have been obtained by Wedekind and Schenk, Ber. 1911, 44, 198, and Staudinger and Pfenninger, Ber. 1916, 49, 1941.

Diphenylmethane mono-, and dicarboxylic acids have been prepared by Mitter, Ber. 1912, 45, 1207, by the action of oxalyl chloride in presence of aluminium chloride on diphenylmethane.   J. B. C.

DIPHENYLMETHYLAMINE. *Methyldiphenylamine v.* DIPHENYLAMINE.

DIPHENYLTOLUQUINOXALINE *v.* AZINES.

DIPICOLINIC ACID *v.* BONE OIL.

DIPLOSAL. The salicylic ester of salicylic acid $OH\cdot C_6H_4\cdot COO\cdot C_6H_4\cdot COOH$, a white crystalline powder, m.p. 147°; almost insoluble in water and dilute acids. Used in the treatment of rheumatic diseases (*v.* SYNTHETIC DRUGS).

DIPPEL'S OIL *v.* BONE OIL.

DIPROPÆSIN. A derivative of urea containing the residues of 2 mols. of propæsin.

DIPROPYLACETIC ACID *v.* OCTOIC ACIDS.

DIPYRIDINE *v.* BONE OIL.

DIPYRIDYL *v.* BONE OIL.

DIRECT BLUE, -BROWN, -GREY, -INDONE BLUE, -ORANGE, -ROSE, -YELLOW *v.* AZO-COLOURING MATTERS.

DISALOL. Trade name for phenyl salicylsalicylate.

DISAZO- and TETRAZO- COLOURING MATTERS. The terms 'disazo' and 'tetrazo' are both used to indicate the presence of two azo- groups ($\cdot$N:N$\cdot$) in the molecule of a colouring matter, but at the same time they indicate the mode of preparation of such dyestuffs rather than, strictly speaking, their constitution. Tetrazo- colouring matters may be regarded as a special division of the disazo-colouring matters, as will be seen from the following classification.

Primary disazo-colouring matters are obtained by the action of two molecules of a diazo- compound (derived either from two molecules of an amine or from two different amines) on one molecule of an amine (e.g. m-phenylenediamine, m-tolylenediamine), a phenol (e.g. phenol, resorcinol, a dihydroxynaphthalene) or an aminophenol (e.g. aminonaphtholsulphonic acids). The position taken up by the diazo- groups may be illustrated by the commonest cases (see also Azo- colouring matters). m-Phenylenediamine : The azo- groups occupy the two positions para- with respect to the two amino- groups. When one of these para- positions is occupied, as in m-tolylenediamine, the second azo- group enters the ortho- position with respect to the second amino- group ; thus :

$$CH_3 \underset{NH_2 \quad N_2}{\overset{N_2-}{\underset{\qquad}{\bigcirc}} NH_2^{\cdot}}$$
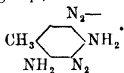
Phenol, a-naphthol. The para- and ortho-positions with respect to the hydroxy- group are occupied.

Resorcinol. Two isomeric disazo- dyestuffs may be formed. When the combination is effected in alkali hydroxide solution, the symmetrical compound (I.) is obtained, but when

$$\underset{I.}{HO\overset{N_2-}{\underset{\bigcirc}{\bigcirc}}OH} \qquad \underset{II.}{HO\overset{N_2-}{\underset{\bigcirc}{\bigcirc}}OH}$$
$$-N_2 \qquad \qquad N_2- \qquad \qquad N_2-$$
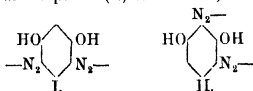
the reaction takes place in the presence of sodium acetate or sodium carbonate, the unsymmetrical compound (II.) is produced.

Dihydroxynaphthalene. Here the azo- groups enter the usual position with respect to the hydroxy- groups, as would be expected if these groups represented two independent naphthols (cf. Azo- colouring matters).

Aminonaphtholsulphonic acids. In this case also, the compound may be regarded both as an independent naphthylamine and as a naphthol ; one molecule of the diazo- compound is combined in acid solution, when the position taken up by the azo- group is the same as if the substance were a naphthylamine, and the second molecule is combined in alkaline solution as if the substance were a naphthol.

Secondary disazo- colouring matters are obtained by the action of a diazoazo- compound on an amine or phenol ; their general formula is $X \cdot N_2 \cdot Y \cdot N_2 \cdot Z$, the essential difference being that Y does not contain primary class auxochrome groups (NH_2 or OH).

Tetrazo- colouring matters are produced from diamines, both amino- groups of which are diazotised (i.e. the diamine is tetrazotised) and combined with two molecules of the same or different components (amines or phenols). These are mostly derived from benzidine, tolidine, dianisidine, &c. ; some, however, are prepared from p-phenylenediamine, and in this case direct tetrazotisation cannot conveniently be effected, but the monoacetyl compound is first diazotised and combined, the acetyl- group being then eliminated and the free amino- group is diazotised and combined with the second molecule of a component.[1] When the first combination has been effected with an amine (in practice nearly always a naphthalene derivative), and in consequence a diamino- compound is produced on saponification, treatment with one molecule of nitrous acid leads to the diazotisation of the benzenoid amino- group, that attached to the naphthalene ring not being attacked.

For the sake of completeness, it is necessary here to describe those dyestuffs which contain three or more azo- groups.

Trisazo- colouring matters are obtained in the following ways. (1) Combination of three molecules of a diazo- compound with a phenol. This method is of only theoretical importance, and has hitherto been applied only to the cases of phenol (Wallach and Fischer, Ber. 1882, 15, 2814 ; Grandmougin and Freimann, ibid. 1907, 40, 2662 ; J. pr. Chem. 1908, [ii.] 78, 384 ; Heller and Nötzel, ibid. 1907, [ii.] 76, 58 ; Heller, ibid. 77, 189), phloroglucinol (A. G. Perkin, Chem. Soc. Trans. 1897, 71, 1154), and resorcinol (Orndorff and Ray, Ber. 1907, 40, 3212 ; Amer. Chem. J. 1910, 44, 1). (2) Combination of one molecule of a diazoazo- and a diazo- compound with a phenol, amine, or aminophenol. The diazoazo- compound may be produced, for example, by diazotising an aminoazo- compound such as p-sulphobenzeneazo-a-naphthylamine, or the intermediate product, obtained by combining a tetrazotised diamine (benzidine, &c.) with one molecule only of a component (such as salicylic acid, &c.), may be used, or the formation of the diazoazo-compound may be left to the last stage of the operation, for example, a tetrazotised diamine (benzidine) may be combined with one molecule of an aminonaphthol (H acid) in acid solution, a diazo-compound (diazobenzene) now added in alkaline solution and the diazodisazo-compound coupled with a component (m-phenylenediamine or phenol) (Eric direct black GX and Eric direct green DT). (3) Combination of a diazotised tetrazo- colouring matter (which must, of course, contain a diazotisable-amino- group) with a phenol or amine, either in substance or on the fibre. (4) Combination of a triamine (e.g. magenta), having each amino- group diazotised, with three molecules of a component.

Tetrakisazo- colouring matters, containing four azo- groups, are obtained (1) by the combination of two molecules of a diazoazo- compound with a phenol or amine (e.g. Anthracene acid brown B, v. Azo- colouring matters) ; (2) by combining two molecules of a diazo- compound with one of a tetrazo- colouring matter (e.g. Benzo brown G) ; (3) by combining a tetrazo- compound, with two molecules of a monoazo-colouring matter (e.g. Hessian brown BBN) ;

[1] An alternative method is first to combine diazotised p-nitroaniline with the component, then to reduce the nitro- group with sodium sulphide, and diazotise the amino- group thus formed.

(4) by tetrazotising a tetrazo- colouring matter (containing two diazotisable amino- groups) and combining with two molecules of a component (*e.g.* Dianil black PR) ; (5) by diazotising a tris-azo-colouring matter (containing one diazotisable amino- group) and combining with a phenol or amine either in substance or on the fibre.

Colouring matters, containing more than four azo- groups, can be prepared, but, generally speaking, their tinctorial power is little or no greater than those described above.   J. C. C.

DISINFECTANTS. A disinfectant is an agent that will kill lower organisms which act injuriously on the higher forms of life. Although most disinfectants are also antiseptics and deodorants, a clear difference between the three classes lies primarily in their uses and objects. Disinfectants are germicides : antiseptics may only retard or inhibit the growths. It is not essential for a disinfectant to effect absolute sterility : in practical disinfection, there is nearly always a residue of highly resistant and non-pathogenic organisms. To destroy these involves great additional time and cost, and may even be disadvantageous when they act as natural scavengers in removing objectionable organic matter and antagonising dangerous forms. The choice of an agent will obviously depend on considerations of safety, convenience, and economy in use

INORGANIC SUBSTANCES.

Ordinary oxygen acts slowly by the aid of aërobic organisms. Its activity is slightly increased by compression ; it becomes exceedingly energetic when converted into **Ozone.** Since ozone is decomposed by heat and absorbed by most metals and by otherwise inert organic matter, the chief conditions for success and economy in working are (1) avoidance of sparking ; (2) keeping the gas and the apparatus cool ; (3) straining the air, and also partially drying when it is desired to prevent the formation of oxides of nitrogen ; (4) parts in contact with ozone must be made of, or lined with, unoxidisable materials ; (5) the grosser organic impurities, as well as sulphuretted hydrogen and ferrous iron, should be removed before disinfection. The use of ozone on the large scale for purifying water is now well known, and the principal types of apparatus have been described by Don (Inst. Mechan. Engineers, Jan. and Feb. 1909 ; *see* also S. Rideal, J. R. San. Inst. 30, 1, 1909 ; Rideal found at St. Maur Waterworks, Paris, that with the sand-filtered (Marne) river water, containing a fluctuating number of bacteria, 28-320 per c.c , with a mean frequency of *coli* organisms of 1 per 100 c.c. (in more than one-third of the tests it was 1 in 40 c.c.), ozone in the proportion of about 0·6 gram per cubic metre of water (6 lbs. per million gallons) destroyed all bacteria except an average of 1 per c.c. of innocuous spore-bearing organisms of the *subtilis* type. The ozonised air was applied in a De Frise tower at the rate of about 40 p.c. of the volume of water treated, and contained 1·4–1·8 grams of ozone per cubic metre (determined at frequent intervals by neutral potassium iodide). An advantage of ozone is that in disinfecting it adds no mineral matter to the water, and it has been fully proved that where water is not too contaminated

with organic matter, sulphuretted hydrogen, or ferrous iron, ozone will destroy all pathogenic organisms at a reasonable cost. In the dry state, like chlorine, it has very little action on micro-organisms, and therefore does not act powerfully on bacilli in air. 8 grams per cubic metre of air in a room ordinarily closed accomplish disinfection in 3 hours. Its use as an adjunct to ventilation has often been proposed, but its irritant action on the lungs prohibits its use in these quantities. It is most active when moist. Ozonised air, under pressure, has been used successfully for destroying moulds and bacteria in brewers' foul casks, and has been introduced into wort in the latter part of the fermentation ' to destroy noxious germs ' (Eng. Pat. 22355, 1898) Will and Beyersdorfer (Zeit. ges Brauw. 1912, xxxv. 73) showed that air containing 0·6–0·7 gram of ozone per cubic metre destroyed organisms inimicable to the brewery. On account of its rapid consumption by oxidisable substances, it can only be effective in disinfecting the *surfaces* of organic solids. At the Pittsburg Homœopathic Hospital, ozone, besides purifying the water supply, is used for sterilising instruments, bandages, &c., and for dressing wounds and ulcers. In cold storage it would probably be useful for destroying injurious organisms and odours, thereby possibly lessening the amount of refrigeration required. Many attempts have been made to utilise it for disinfecting, combined with bleaching, textiles, feathers, and other surface-contaminated articles, and have been only limited by questions of expense.

Patent 4153 of 1902, for ' fixing ozone in liquids,' states that pure acetaldehyde dissolves 2823 times its volume of ozone ; that 10 p.c. solutions of acetaldehyde in water dissolve 536, in alcohol 748, in ether 859 volumes of ozone ; that these solutions are very stable, and have been successfully used in surgery.

Hydrogen peroxide. The first experiments (Ber. 15, 1585) showed that this was a bactericide which, in the dilute state, appeared inert to enzymes such as diastase,[1] ptyalin, pepsin, and pancreatin ; did not injure foods ; and is also innocuous and non-corrosive. These properties suggested its use for killing pathogenic organisms, and those that cause change in articles of diet, especially milk (Renard), and also as an internal disinfectant. Altchoefer (Centr. Bakt. 1890, viii. 129) and most later observers give 1 per 100 of H_2O_2 as required to destroy pathogenic organisms in 24 hours. In 1903 S. Rideal found that in milk raised to 50°, then treated with 0 6 gram of H_2O_2 per litre, and the heat maintained at 52°–55° for 8 hours, pathogenic organisms and even the spores of *B. anthracis* and *subtilis* were killed, the milk was not physically altered, and kept for over a month unchanged in the closed receptacles (Budde's patent 10903, 1903). Similar results have been obtained by Lewin and others, by Hewlett (Lancet, Jan. 27, 1906), and Reichel (Zeit. f. Hyg. 1908, lxi. 49). So that hydrogen peroxide aids pasteurisation, and enables it to be efficient at a lower temperature. The solution is

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[1] The enzyme *catalase* (present in malt, yeast, milk, and many organic liquids) and hydrogen peroxide mutually decompose one another (Van Laer, J. Soc. Chem. Ind. 1906, 489 ; 1909. 950) ; but the above statement remains practically true. (*See also ibid.* 1909, 1267.)

frequently used as a spray, gargle, or dressing, and has had a wide application for war service in dealing with gas gangrene infected wounds (*see* reports by Capt. M. Page, R.A.M.S., Lancet, Sept. 1914; Col. Makins, *ibid.* August, 1914). Peroxide of hydrogen is present in 'Sanitas' (*q.v.*). 'Perhydrol' is a 30 p.c. or 100 volume solution of H_2O_2. The use of peroxide of hydrogen in medicine depends partly on its bactericidal action. Registered names of solutions are 'Dioxogen' (3 p.c.), 'Hydrozone,' 'Glycozone' and 'Pyrozone' (dental practice); and 'Peroxols' are mixtures of H_2O_2 with various disinfectants. Peroxides of sodium, magnesium ('Hopogan'), zinc ('Ektogan' or 'Dermogen') and mercury, generate oxygen or H_2O_2, and have analogous use. Hydrogen peroxide is more stable in ether than in water; 'ozonic ether' is an ethereal solution containing about 1·2 p.c. of H_2O_2, which has been used in whooping-cough and scarlet fever. 'Perhydrit' or 'Hyperol' dressings, containing H_2O_2, urea, and a trace of citric acid, have recently been introduced.

Foregger and Philipp (J. Soc. Chem. Ind. 1906, 298) treat at length on the applications of peroxides, and suggest calcium peroxide ('Bicalzit') instead of H_2O_2 for sterilising milk, as more lasting in effect. For water sterilising, tablets of magnesium peroxide and citric acid are made; Park found that 0·1 gram of this peroxide killed upwards of 2 million typhoid organisms in 150 c.c. of water in 30 minutes, and 0·2 gram gave the same result in 1 minute. Although Cronor (Zeit f Hyg 1908, lvii. 487) obtained sterility in water with the use of 0·7–1·0 gram MgO_2 per litre, more recent investigations by Young and Sherwood (J. Ind. Eng. Chem. 1911, 3, 495) have indicated that over five times this quantity must be used to ensure sterility. Patents for similar uses of H_2O_2 and other peroxides are very numerous.

Nitric acid and oxides of nitrogen. The corrosive action of nitric acid limits its value as an active disinfectant J. C Smith used it with success in 1780 for fumigation in a violent outbreak of *typhus* fever in the British fleet (Vallin, Désinfectants, 1882, 265). Disinfection of rooms by nitrogen peroxide was carried out during the siege of Paris ; 48 hours were occupied, and the cost was very high. Severe bronchitis and several deaths from poisoning have resulted from breathing this gas, and nitric disinfection has been replaced by safer methods, except in the local destruction of bacteria as in laboratories.

Sulphur. Dusting with sulphur is used for killing insects and fungi on plants, as sulphurous acid is gradually formed. The use of sulphur internally is due to its forming sulphuretted hydrogen in the system, and thereby destroying or enfeebling micro-organisms and higher parasites. A solution containing calcium polysulphides, made by boiling milk of lime with sulphur, has been extensively used as an insecticide (*see* Agric. Bull. 319 and 320, New York, 1909).

Sulphur dioxide disinfection is still a subject of controversy, but certain of the unfavourable results adduced have been due to faulty application. Spores are not generally killed by it, and the dry gas has very little effect on micro-organisms, but it destroys all vermin, and therefore is of special value in combating insect-borne

diseases. As to its effect on the lungs, about 5 p.c. in the air has produced fatal results, but $\frac{1}{2}$ p.c. can be tolerated for some time, and a larger amount with the protection of a wet towel alkalised with washing soda. 1 lb. of sulphur burnt in a room of 1000 cubic feet produces theoretically an air-content of 1·15 p.c. SO_2, and requires 0·56 lb. of water to turn it into sulphurous acid. Such an amount of moistening is, however, not necessary, on account of the natural moisture of the air. Prescriptions as to the proper quantity of SO_2 have varied greatly, partly because in some cases it has been considered sufficient to destroy only a special organism. Klein, Houston, and Gordon (Report, Med. Off. L.C.C. 1902) found that with $3\frac{1}{4}$ lbs. S per 1000 cubic feet in 24 hours, *B. typhosus*, *diphtheriæ*, *pyocyaneus*, and *Staph. p. aureus* were killed, but not anthrax spores nor *B. tuberculosis* in dried sputum. In America, 5 lbs. per 1000 cub. feet have been found sufficient to kill all spore-bearing organisms after 16 hours' exposure (Rosenau) S. Rideal's results with the liquefied gas were as follows. Silk threads and paper slips infected with *B. coli* and *Staph. p. aureus* were sterilised after 24 hours' exposure in a sealed room of 1500 cub. feet, into which 20 ozs. of SO_2 were passed. *Subtilis* spores were not killed. With 10 ozs., the threads were again sterilised, but the paper slips were not. When shallow pans of water were exposed in the room to supply moisture, the SO_2 content of the air was actually *lowered* after the 24 hours (through absorption by the water), from 0·5 p.c. present in the previous experiment to 0·2 p.c., and the organisms were still living. Therefore moisture should only be supplied by washing or lightly spraying the surfaces. In chemical disinfection, it is generally recommended that walls should be previously stripped and fabrics spread out on lines; but spreading the infection must be carefully avoided. The room must be sealed by obvious means, and, observing this condition, heating is advantageous. Liquid SO_2 in canisters is more convenient than burning sulphur, and avoids risk of fire : one pound of the liquid $= 5\frac{1}{2}$ cub. feet of the gas. SO_2 has the disadvantage that it attacks metals and organic substances from the production of sulphuric acid : a good deal is also absorbed by plaster. It has little penetrating power, and therefore bedding and thick articles must be removed and sterilised by heat. The 'Clayton method' of disinfection is much used for the holds of ships, and has been favourably reported on by Wade and Eyre for the Local Government Board (Rep. 232, 1906; and Med. Off. Rep. 1903-4, 330). Sulphur is burnt in a special apparatus, and the gases, consisting of air, SO_2, and a visible cloud of sulphuric acid, are forced in till the SO_2 reaches about 10 p.c. of the air in the infected space. (For experience of its use, *see* Rev. d'Hyg. Oct. 1902; N.S.W. Agric. Gaz. 1900 and 1901).

• Sulphurous acid is used beneficially as a germicidal spray or wash in various parasitic affections (*e.g.* diphtheria), also internally in cholera and gastric fermentation, for rectal injections, and other allied objects. 'Thiocamf' is a liquid obtained by the action of the gas on camphor. It can be preserved without pressure in well-closed vessels, and on exposure to air a 6-oz. bottle should evolve about 20 litres of SO_2.

Sulphurous acid and bisulphites are widely used for checking fermentations and preserving food. Lehmann states that an amount equivalent to 0·004 p.c. of SO$_2$ may be allowed without injury to health. The Report of the British Departmental Committee on Preservatives, 1901, 26, leaves the matter open. Some commercial preparations are 'Meat preserve crystals,' 'Freeze-em,' and 'Hawke's anti-ferment.' For objections to the use of sulphites in food, *see* Thresh and Porter, Preservatives, 1906, 70–77; also an article by Durham in the J. of Hygiene, April, 1909. The latter recommends the fixing of a maximum legal limit, not exceeding 0·01 p.c. of 'total sulphur dioxide,' with a declaration of the amount, but less than 0·001 or 0·002 p.c. might be simply declared as a 'trace.'

Sulphuric acid, like acids generally, is antiseptic, and in some cases disinfectant. 0·05 p c. (which is a palatable strength) is fatal to *Sp. choleræ* in 15 minutes. Stutzer found that this strength disinfected iron pipes, cleaning out rust and sediment without sensibly attacking the metal. With 0·04 p.c. Ivanhoff destroyed cholera organisms in Berlin sewage, and with 0·08 p.c. in that from Potsdam. In the laboratory it was found that 0·035 p.c. kills *B typhosus* in 30 minutes, and 0·07 p.c. in 15 minutes, in impure water infected ordinarily with typhoid, but with very heavy infections the latter strength requires 45 minutes. He recommended 0·09 p.c. as having advantages over heat sterilisation for dealing with the drainage from hospitals and other infected areas : the acidity would speedily be neutralised on mixing with the bulk of the sewage (Brit. Assoc. 1901).

Sodium bisulphate has been introduced by one of the writers and Dr. Parkes, as a means of sterilising drinking water for armies in the field and travellers. 15 grains of NaHSO$_4$ to a pint of water in 15 minutes destroys *B. typhosus* and *enteritidis*, *Spirillum choleræ*, and internal parasitic worms. In effervescent tabloids, yielding a slightly acid solution, it was used with success in the South African, Russo-Japanese, and the European wars.

Persulphates give off oxygen when moist, and are useful as hand disinfectants (Lancet, 1905, ii. 1106).

Carbon disulphide, if it were not for its other properties, would be a valuable disinfectant and preservative. As well as its alkaline compounds, the xanthates, it has been found useful against fungi, and insect parasites such as the vine phylloxera. Ckeandi Bey's lamp burns it safely for generating SO$_2$.

Boric acid is not a disinfectant, but has a power of restraining bacteria which act injuriously in foods. Rideal and Foulerton found that 1 in 2000 of a boric mixture, containing 3 parts of H$_3$BO$_3$ and 1 part of crystallised borax, keeps milk sweet for 24 hours without appreciable effect on digestion. The British Departmental Committee already referred to, recommend that the only preservatives allowed to be used in cream, butter, and margarine be boric acid, or mixtures of boric acid and borax, not exceeding 0·25 p.c. of H$_3$BO$_3$ for cream, and 0·5 p.c. for butter and margarine. Later, as this quantity appeared insufficient in the cream trade, an official report by Hamill advised that 0·4 p.c. H$_3$BO$_3$ should be allowed in cream from

May to October inclusive (Food Report 10, L.G.B. 1909). Soluble borates are used as a larvicide in manure heaps. It has no action on the crops as they are rendered insoluble (Cook and Wilson, J. Agric. Research, 1917, 10, 591).

The Halogens, chlorine, bromine, and iodine, act as disinfectants in several ways : (1) they can combine with H$_2$ and liberate O$_2$ in water ; (2) they can combine directly with organic matters, or replace the hydrogen in them, precipitating albuminous substances and rendering them imputrescible, killing organisms by combining with and coagulating protoplasm, removing their food or rendering it unsuitable, acting toward them as irritants or direct poisons, also producing substances which have that effect.

Chlorine and the hypochlorites, like other oxidisers, are consumed by otherwise inert organic and inorganic matters present, but in ordinary disinfection leave behind them as substitution compounds which maintain germicidal power—the chloramines, hydrazine, and the chloroproteids (Rideal, J. R. San. Inst. 31, 2, 1910). This paper shows that in dilute solution of hypochlorites the Rideal-Walker coefficient of 2·18 for 1 p c. of available Cl is increased to 6·36 by the addition of an equivalent of ammonia, remains near this level for 24 hours, and even after 72 hours has an enhanced value. Therefore, since the coefficient of chlorine itself averages 220 units, that of ammonia less than 0·7, and ammonium chloride *nil*, that of the chief product, *chloramine* NH$_2$Cl, must be over 600 units ; hence this substance, but for its instability, would probably be the most valuable of disinfectants. It has a pungent odour, hitherto often mistaken for chlorine or hypochlorous acid, and gives the blue reaction with KI and starch. With excess of ammonia, as in sewages, it gradually disappears, forming a salt of *hydrazine,* which still has a germicidal value (R. W. coefficient of the base at least 24). The action of chlorine on nitrogenous compounds gives compound chloramines, many of which are insoluble ; they have a tendency to become fixed on cellulose, and in this way attack the envelopes of organisms.[1]

Various substituted chloramines have been introduced by H. D. Dakin for use as sterilisers and disinfectants. Amongst the more important may be mentioned chloramine-T, *p*-toluene sodium sulphochloramide, *p*-sulphodichloraminobenzoic acid, and dichloramine T (B.M.S. Aug. 1917). The former, under the title Halozene, has been used for water sterilisation on a small scale.

The addition of ammonia solutions to bleaching powder solutions preparatory to the sterilisation of water has effected a considerable economy in the quantity of materials used in the public water supply at Toronto, Canada.

The chloramine is about five times as strong as the corresponding molecular concentrations of sodium hypochlorite.

· The bromamines of the benzene series, the naphthaline chloramines and the protein chloramines, are all strong germicides, but suffer from lack of stability in solution.

Chloride of lime, or 'calx chlorinata ' (about 33 p.c. available chlorine), has some advantages

[1] Also see Cross Bevan and Bacon, Chem. Soc. Trans. 1910, 244.

from being a solid, but is quickly deliquesced and decomposed by air, takes some time to dissolve, and gives a quantity of insoluble waste. Klein found that 1 p.c. of bleaching powder only killed less resistant organisms in 24 hours. There is, in many respects, a preference for the sodium solutions: chlorinated soda or 'Eau de Labarraque' (often called 'Eau de Javel,' which was originally the potash salt), contains about 2·5 p.c. av. Cl; 'Chloros,' 10 p.c. av. Cl; 'Antiformin' is a solution of caustic soda and hypochlorite used in breweries. Electrolytic preparations are 'Oxychloride,' up to 11·5 p.c. av. Cl, and 'Hermite fluid,' used successfully at Poplar. In the latter solution magnesia is employed as an adjunct in the electrolysis: it contains free hypochlorous acid: av. Cl 4·2 to 4·8 p.c. The effective strength for local disinfection is 0·35 p.c. av. Cl, which kills nonsaatring organisms in 5 to 10 minutes, and anthrax and enteritidis spores in 1½ hours. Chloride of lime has the objection that it leaves the surface for a long time damp from the presence of calcium chloride. The same salt imparts its bitter taste, and increases the hardness, when chloride of lime is applied to the purification of drinking water, while the soda preparations tend to soften the water and are not sensible in the flavour. In trials at Guildford in 1904 (J. R. San. Inst. xxvi. 891) with electrolytic hypochlorite in the proportion of 0·75 to 1·0 part per million of av. Cl, one of the writers found that water containing an average of 90 organisms per c c. was practically sterilised, while after standing 1½ hours the odour and taste were normal, and there was no need for further treatment. Candy's patent, 4212, 1906, removes excess of av. Cl by filtration through coke, Thresh's, 3023, 1909, by treatment with metallic iron. Other methods of removal are suggested: (1) by the addition of ferrous salts, subsequently removing the ferric salt formed by a 'Permutit' filter; (2) by the addition of gaseous sulphur dioxide; (3) by the addition of sodium bisulphite. After the Maidstone typhoid epidemic, 1897, the infected reservoir, mains, and pipes, were sterilised with 1 p.c. solution of chloride of lime during 48 hours: no corrosion of the iron was observed. During a similar outbreak at Lincoln, in 1905, the water supply was sterilised by sodium hypochlorite (av. Cl, 1 per million) with most satisfactory results. In 1910 Toronto treated its water supply with 0·14 part per million of av. Cl as chloride of lime. Since June, 1909, the writers have been applying 'Chloros' in the proportion of 1 to 2 parts av. Cl per million to 100,000 gallons daily of the drinking water of a town in the north of England: the liquid is made practically sterile, coli is absent from 75 to 85 c.c., and there is no effect on the taste. At Cambridge, in 1910, a portion of the supply (lower chalk) was treated with one in 4 to 8 millions of av. Cl as chloride of lime, and Houston found that this minute quantity destroyed 66 to 98 p.c. of the bacteria, and coli, which was always present before, was afterwards absent in 500 c.c. This water, however, contained hardly any organic matter. In America, treatment of the entire water supply of Jersey City (about 40 million gallons per day, from the Rockaway river) with chloride of lime, has been adopted since the beginning of

1909: the proportion used is now 0·2 part per million of av. Cl, and the daily examination shows that coli is absent from 10 c.c. of the treated water. In England, the 'De-Chlor' system was applied at Reading to the prefiltered river water in 1910. Since the war chlorine treatment has been adopted for the London supply (11th Annual Report, M.W.B.).

Recently an impulse has been given to the sterilisation of water by means of gaseous chlorine injected by means of suitable dosing apparatus, owing to the convenience of handling and transporting chlorine in the liquid state contained in steel cylinders of 100 lbs. capacity. Injection into the water may be direct through a diffuser, as in the Wallace and Tieman apparatus, or indirect through the addition of a minor volume of more concentrated chlorine water to the bulk volume, as in the Electrobleach and Patterson plants. NH₃ does not seem to enhance the germicidal value in the absence of alkaline bases.

With sewage, of course, a larger dose is required, and the first experiments at Nice, Brest, and Worthing, in 1894, with the Hermite fluid, showed that, as with ozone and other disinfectants, the agent should be applied, not to a raw liquid (except in special cases), but as a 'finisher' to one that was partially purified. In 1898, using an electrolytic brine (Woolf's 'Electrozone') for purifying an effluent at Maidenhead, one of the writers found that with three parts per million of av. Cl, and a contact of 5 minutes, the bacteria were reduced to 10 per 50 c c, and that 17 parts per million killed all the organisms in 15 minutes. His long series of trials at Guildford commenced in 1904, using 'Oxychloride,' and proved that with 2·5 parts per million of av. Cl, tertiary effluents could be practically sterilised, but that the raw sewage and septic effluents required 30 to 70 parts; the contact period was 4½ hours (J. R. San. Inst. xxvi. 7, 1905). The oxygen consumed from permanganate in 5 minutes in the cold, as measuring the H₂S and other easily oxidisable substances, was a guide to the amount of the agent used, and in the earlier experiments it was found that when the av. Cl added was 1·7 times this figure, the availability of the chlorine was sufficiently prolonged to ensure the desired sterilising effect, and the subsequent experiments frequently yielded excellent results with an amount equal to this oxygen figure, that is, one to one. (See further, Rideal, Trans. Farad. Soc. iv. 3, 1909.) An important point shown was that the necessary factor of safety could be ascertained by simply testing with KI and starch, and noticing the persistence after 4½ hours of the blue colour, due in this case, as has been mentioned, not to chlorine, but to chloramines. Schumacher (1905), at Hamburg, found that with raw sewage sufficient sterilisation is attained if after 4 or 6 hours the test shows a reaction equal to 19 and 17 parts of million of av. Cl respectively. Investigations on sewage filter effluents with chloride of lime were continued in America by Phelps and Carpenter (U.S. Technological Quarterly, Dec. 1906), who remark that the use of electrolytic chlorine manufactured on the spot would, in the larger works, considerably reduce the cost, and is cheaper than sand filtration. Kellerman, Pratt, and Kimberley (U.S. Dept. of Agric.

Bull. 115, Oct. 1907) conclude that with a hypochlorite, disinfection costs less than with copper sulphate. Later American experiments at several centres have proved that 2 to 5 parts per million of av. Cl destroy 95 to 98 p.c. of the bacteria in 2 hours, and that 3 parts are sufficient for the trickling filter effluents tried (Mass. Inst. Technol. 5, 1909 ; 6, 1910).

The Royal Commission on Sewage obtained results at Guildford which were in agreement with those of the writer (Appendix iv. 1910, 87 ; also ibid. 84-171, and Rep. 1908, 195-201).

Sod. hypochlorite solutions are the best means of sterilising swimming baths ; they remove from the surfaces growths of algæ and fungi which harbour dangerous organisms. (Also see Rideal and Orchard, J. San. Inst. 556, 1906.)

'Ferrochlore' (Duyck) is the name of a treatment with 8 parts per million of ferric chloride and 0·5 part of chloride of lime, which at the same time clarifies water and liberates hypochlorous acid.[1]

Hypochlorous acid has been employed as an antiseptic for wounds by Dakin, Daufresne, and Lorraine Smith, and is also known as 'Eupad' and 'Eusol.' In these solutions hypochlorous acid is obtained by double decomposition of bleaching powder with sodium carbonate, with the addition of boric acid or sodium bicarbonate. The presence of sodium borate or sodium carbonate in the resulting solutions when freed from the precipitated calcium carbonate ensures the stability of the solution owing to the 'buffer' action of the easily hydrolysable salt.

Chlorine peroxide, obtained from potassium chlorate and sulphuric acid, has been successfully employed in the Howatson-Bergé process at Brussels, Ostend, and Lectoure (South France), for sterilising (previously clarified) polluted waters. The writer found that 20 parts of ClO_2 per million did not kill B. typhosus in a vigorous pure culture in 2 hours, but that 50 parts killed it in half an hour. (See also Reychler, Bull. Soc. chim. [3] xxv. 13 ; Chem. News, 1901, 316)

On a large scale, chlorine and ozone are both in successful use at present for sterilising water. The latter seems preferable for drinking supplies, the former is suitable for effluents. From questions of efficiency as well as cost, both require that the liquid should be previously clarified, and as free from organic matter as possible, that is, they are finishers.

Time as in all disinfections, is an important factor ; in an effort to get the work done quickly, it is sometimes forgotten that a longer time is advantageous, and economises the re-agent. For rapid sterilisation of a small quantity, as in the field, a larger proportion of reagent is required, and from questions of portability, bromine and iodine have been used instead of chlorine, but are attended by residual products having a taste and physiological effect. These, in the quantity required for dealing with the moderate pollution ordinarily met with, have been proved to be negligible, although, with heavier contamination, the amount of the halogen consumed by the organic matter before a sterilising excess is present, may become in-

jurious in its products. Cash showed that the quantities of chlorine, bromine, and iodine required for disinfection of anthrax and tubercle were nearly in the ratio of their atomic weights.

Bromine is a powerful disinfectant, but its use is obviously limited by its danger. In 1897 Altmann patented a solution of Br in KBr for sterilising water, using 40 parts per million of Br with 5 minutes' contact, and removing excess by ammonia. The solution is, however, bulky, and the use of a potassium salt has disadvantages. Braithwaite introduced 'Bromidine,' a dry mixture of sodium or potassium bromide and bromate with sodium bisulphate, which with moisture liberates bromine. Schumberg recommended free bromine in thin sealed tubes for the same purpose (Zeitsch f. Hyg. 1900, 53) in the proportion of 60 parts per million with 5 minutes' contact, removing excess by thiosulphate (Braithwaite advised 57 parts). Schöder (ibid xxxvii. 306) and others have stated that this treatment is insufficient to sterilise, and the presence of residual bromides is against the process (see also Parkes and Rideal, Trans. Epidem Soc. xx. 1901 ; Fraser, Publ. Health, Sept. 1902). It was tried in the Soudan campaign of 1898. 20 parts per million of Br sterilises typhosus (in water) in less than half an hour. It is more rapidly absorbed by organic matter than iodine.

Iodine owes many of its uses to its germicidal action, as in parasitic diseases. Grossich, in 1908 (Centr. f. Chirurg No. 4), adopted the tincture as a cutaneous disinfectant before operations, the surface being previously cleansed by a 1 p.c. solution of iodine in benzene (Bogden, ibid. Jan. 15, 1910). Instead of the tincture, Chassevant (Lancet, March 26, 1910) suggests the solution in chloroform, as it does not, like the former, cause desquamation ; its use is specially advised prior to hypodermic injections (see also Brit. Med J. Feb. 6, 1909, and Aug. 14, 1910 ; Lancet, April 16, 1910). Solutions of iodine and iodine trichloride, both as field dressings, and enclosed in friable glass compounds as emergency first-aid sterilisers, have been extensively employed during the war (see B. M. S. Jan. 2, 1915 ; Lancet, Dec. 12, 1914). During the Sikkim and Thibet expedition, iodine (in some cases as tincture) followed by sodium sulphite, was successfully employed for sterilising drinking water, and Nesfield recommends triple tablets of (A) iodide and iodate, (B) citric or tartaric acid, followed after 2 minutes' contact by (C) sodium sulphite, and states that used in this way 3·8 to 5 parts per million of free iodine sterilises the organisms of typhoid, cholera, and dysentery. One of the writers, in 1905, confirmed this result as regards distilled water infected with 20,000 per c.c. of B. typhosus, the A and B tablets used gave 4·75 parts of iodine per million.

Iodine trichloride was introduced by Von Langenbach for sterilising the hands and instruments and for other surgical uses. 50 parts per million are required to kill typhoid (in water) in 30 minutes. Iodine cyanide is said, by Kobert, to be universally destructive to lower forms of life, and is suggested for preserving biological specimens.

Organic substitution compounds of chlorine, bromine, and iodine, as a class, inhibit organisms,

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[1] For an account of trials at Marseilles of ozone, chlorine, and ultra-violet rays, see Engineering, Jan. 27th and Feb. 3rd, 1911.

and may sometimes kill them. The germicidal power of a large number of these has been determined by Bechhold (Zeitsch. Hyg. Infect. 1909, lxiv. 113); he finds that a Br atom gives a greater power than a sulphonic group. *Chloroform* is often used to preserve perishable specimens and infusions. Farrel and Howles (J. Soc. Dyers, 1908, 24, 109) state that CCl_4 kills typhoid, and that pure $CHCl_3$ does not kill it, whilst 0·62 p.c. aqueous $CHCl_3$ kills it in less than 30 minutes.

Iodoform was formerly much employed in surgery, and a large number of other iodine compounds have been introduced into medical and surgical practice. Many of them are non-irritant, but their bactericidal power is much inferior to that of dilute solutions of the element. Fumigation of sick rooms with iodine, sometimes in conjunction with other disinfectants, by burning prepared candles or lamps, has been tried, but apart from the fact that the method is unsatisfactory, no chamber can be disinfected while occupied.

The organic iodo- compounds owe most, if not all, their germicidal power to the gradual liberation of iodine by the alkaline wound secretions. Iodoform itself gives rise to symptoms of poisoning owing to the too rapid evolution of iodine. Amongst the more important organic iodine derivatives may be mentioned hexamethylenetetramine compounds, chrysoform, iodoformin, phenol, and homologous compounds, aristol, iodothymoloform, europhen, traumatol, isophen, iodoamsol, iodocol, iodised albumen, tannin, gelatine, casein, gluten peptone lecithin, and various iodised oils have been protected under fancy names.

Fluorides, like boric acid, check bacteria, but do not kill them. As food preservatives, they are only moderately efficient, and are not innocent physiologically, as they hinder pancreatic digestion. Sodium silicofluoride ('salufer') and borofluoride ('pyricit') have been tried. Effront introduced the use of hydrofluoric acid and its acid salts for checking injurious fermentation, and J. Brand (Zeitsch. f. Brauw. 1904, xxvii. 115) states that 0·5 to 1 p.c. solution of acid ammonium fluoride is largely used for disinfecting rubber hose in breweries (*see also* Hehner, Analyst, 1902, 173; Richmond, Dep. Comm. on Preservatives, appendix xxxi.; Thresh and Porter, Preservatives, 1906, 87). Hydrofluosilicic acid is the active constituent of 'Montanin' (obtained from by-products in the pottery industries), and 'Keramyl' (about 25 p.c. H_2SiF_6) (J. Soc. Chem. Ind. 1904, 34; 1909, 904). Frank (Wasser u. Alwasser) recommended the use of aluminum silicofluoride for water sterilisation. They are stated to have no injurious action on health (Public Health, Oct. 1908).

Carbonic acid seems to have a certain amount of disinfectant action, since 'aërated' beverages have been shown to be in many cases sterilised, and CO_2 under pressure preserves food (*cf.* J. Soc. Chem. Ind. 1907, 1290).

Cyanogen and hydrocyanic acid are more destructive to insects than to lower organisms. Fumigation of fruit trees with HCN is extensively practised in America, and is considered better than spraying. For greenhouses, zinc capsules containing sodium cyanide are made; they are placed in dilute sulphuric acid,

and while the zinc dissolves the operator has time to retire.

Acids. An acid medium is unfavourable to the growth of most bacteria, and acids generally possess considerable disinfectant power. Kitasato found that the growth of *B. typhosus* in nutrient broth or gelatine was entirely prevented by the following percentages of different acids: 0·08 H_2SO_4; 0·2 HCl or HNO_3; 0·28 SO_2; 0·3 to 0·4 phosphoric, acetic, carbolic, formic, oxalic, or lactic; 0·476 tartaric, citric, and malic; 1·66 tannic; and 2·7 boric. One of the writers has shown that in infected waters, 0·035 p.c of H_2SO_4 kills typhosus in 30 minutes, that in terms of acidity nitro-hydrochloric was slightly more active, and that with tartaric and citric at least three times the amount of acidity was required (Epidemiological Society, Jan. 1901). But like other disinfectants, the activity of dilute acid solutions is considerably modified by the presence of added matters; for instance, in 1 p.c. peptone broth, *Sp. cholerœ* is killed by 0·01 p.c. hydrochloric acid in half an hour, but in 2 p.c. peptone broth, 0·04 p.c. HCl is required.

Paul, Kronig, and Sawey (Pharm. J. 1900) conclude that the germicidal activity of acids generally, depends upon the degree of ionisation in solution, exceptions being HF, HNO_3 and trichloracetic, which exercise specific toxic influences. In normal solutions, the three latter killed anthrax spores exposed on garnets in 24 hours, while H_2SO_4, HCl, HBr and $HClO_3$ were less active. Working with more dilute acid solutions, Winslow and Lochridge (Mass. Inst. Tech 1906) have compared the effect on *B. coli* and *typhosus* in tap water and in a 1 p.c. peptone water. With upwards of 10,000 organisms per c.c., sterilisation was obtained by the following percentages of each acid after 40 minutes' contact :—

	B. typhous		*B. coli*	
	Tap water	1 p.c. peptone water	Tap water	1 p.c. peptone water
Hydrochloric acid	0·018	0·174	0·045	0·368
Sulphuric ,,	0·022	0·188	0·081	0·530
Acetic ,,	—	—	0·561	0·836
Benzoic ,,	0·069	0·292	0·242	0·555

In agreement with the results of other workers, larger amounts of each acid are required to disinfect in the presence of peptone; with the organic acids, benzoic and acetic, this diminished activity is not so pronounced. Winslow and Lochridge find that the disinfectant power of the acids is not proportional to their strength in terms of normality, but, in the case of the mineral acids, hydrochloric and sulphuric, to the degree of ionisation of the solution, 99 to 100 p.c. reduction of *B. coli* or *typhosus* being effected with either acid at the same concentration of dissociated hydrogen. The evidence tends to show that the alteration in ionisation in a dilute acid solution brought about by the presence of otherwise inert substances in solution, as, for example, neutral salts of the acid, accounts for the variation in germicidal activity. In practical disinfection, the subject is often rendered still more complex by a further interference—the absorptive effect on solids in suspension. Therefore the acidity, as found by titration, does not give the germicidal value of an acid solution unless these disturbing factors are considered.

Metallic derivatives. Warm alkaline leys are the most ancient of disinfectants : potassium and sodium hydroxides are sterilisers in the proportion of not less than 2 to 5 p.c., their carbonates in 5 to 10 p.c. At 60° a contact of 5 minutes ensures the death of most organisms (Zeitsch. f. Hyg. 1903, 349), hence ordinary soaps have a slight disinfectant value. Strong brine is preservative, but not disinfectant, and the practice, formerly frequent, of washing out milk cans and other utensils with it, is not a safe one. Lode shows (Chem. Zentr. 1902, i. 1122) that 50 p.c. salt solution does not kill the spores of common moulds.

Lime, as quicklime, is fatal to bacteria when it comes in contact with them in an almost dry condition, and has been much used where there is a considerable space and bulk of material to be dealt with. It is not safe, however, to trust entirely to the old method of burying infected bodies in lime, as, on disinterring, the live spores may again be diffused, unless a long period has elapsed. The disinfecting power of milk of lime and whitewash has been much overrated ; as to milk of lime, Liborius stated (Zeitsch. f. Hyg. ii. 25) that in the proportion of 74 parts per million of CaO, it destroyed typhoid bacilli, and that 246 parts per million were required for cholera organisms, while 2 p.c. of dry lime was needed for cholera discharges ; with in each case ' a few hours' ' contact. When lime is added to sewage, a great number of bacteria are carried down, but are not killed, and the supernatant liquid is not sterilised. Dr. Houston (7th and 8th Reports of the Metropolitan Water Board, 1911 and 1912) found that 0·02 p.c. of quicklime effectively destroyed *B. coli* in raw Thames water in from 5 to 24 hours. *Zinc chloride,* ' Burnett's fluid,' formerly in high repute as a disinfectant, is not reliable in its effect, and ranks below copper sulphate and mercuric chloride. The sulphate has still less energy (R. W. coeff. 0·09).

Aluminium chloride, ' chloralum,' was classed by Miquel between zinc chloride and copper sulphate. *Iron salts,* especially ferrous sulphate, were at one time in vogue for sanitation, but are ineffective.

Permanganates and manganates were first introduced as Condy's red and green fluids. Like oxidisers generally, they are largely consumed by otherwise inert matters before attacking organisms, and as complete disinfection cannot be ensured unless an excess of reagent remains, evidenced by a pink colour, which is not always easily visible owing to the brown oxide of manganese produced, their use may be very costly and its execution frequently imperfect. The writer carried out experiments in street-watering of two similar areas of ordinary soiled asphalt roadway : (*a*) with water alone ; (*b*) with permanganate solution 1 in 5000 (six times the amount then customary), and examined the liquid from the surface. The permanganate was almost immediately decolourised. Sample (*b*) was nearly inodorous, on keeping became much less foul than (*a*), and the reduction in the number of organisms was 96 p.c., but the survivors included a large proportion of the dangerous forms (Rideal's Sewage, 1906, 117). For polluted water Rosenau recommends adding permanganate drop by drop till the pink colour

persists for 24 hours. ' Pinking ' of wells was many years ago adopted by Hankin in India as a precaution against cholera. Permanganates, used in various ways, are still being patented, chiefly for water purification.

Chromic acid, although a powerful oxidiser and instantly coagulating albumen, is excluded by its cost and poisonous and corrosive nature from the list of useful disinfectants or of preservatives.

Arsenic, like cyanogen, has more effect on higher than on lower forms of life, and is the basis of valuable insecticides, such as the sheep-dip solutions of arsenious oxide or sulphide in soda, frequently associated with tar products and nicotine. *See* Chemist and Druggist, June 11, 1904 ; Rep. Dept. Comm. B. of Agric., leading to the Sheep-Dip Act of 1903 ; and Quibell, J. Soc. Chem. Ind. 1907, 1266. The copper compounds, ' *Paris green* ' (aceto-arsenite) and others, are used for spraying or dusting trees, combining the actions of arsenic and copper Several organic arsenic compounds have been introduced as medicinal parasiticides (*see* Lancet, Brit. Med. J., &c., 1910 and onwards).

Arsenicals and similar organic metallic compounds are frequently selectively germicidal. Salvarsan, *p-p*-dihydrosia, *m-m*-diamino arsenobenzene has a strong antiseptic action on anthrax, erysipelas, and glanders, as well as syphilis. The selective action is more pronounced in serum (Zeitsch. f. Hyg. u. Infeht. Krankh. 1914, 77).

Among the more important arsenicals may be mentioned :—

Salvarsan.
Cacodylic acid and its salts
Atoxyl sodium aminophenylarsenate.
Asyphil mercury aminophenylarsenate.
Arrhenal methyl disodium arsenate.
Arsacetin *p*-acetyl aminophenyl sodium arsenate.
Soamin sodium arsanilate.
Neosalvarsan sodium 3·3-diamino-4 4'-dihydroxy arsenobenzene methanal sulphoxylate.

Some metals in the free state are antagonistic to germs. Dievert states (Compt. rend. 136, 707) that agitation with granulated zinc kills *B. typhosus* and *coli* in a few hours, and Baeyer's method of treating polluted waters with zinc-dust, charcoal, and lime causes, according to Margosches (Leipz. Monats. Textilind. 1901, vi.), practical sterilisation. Rankin (Proc. Roy. Soc. 1910, B, 82, 78) shows that clean strips of Al, Zn, or Cu, in air-free water, do not reduce the number of *coli*, whilst when air is bubbled through there is a great reduction after 1 hour. Except with Cu, peroxide of hydrogen was produced, but the amounts of this and of the metal dissolved were too small to account for the germicidal effect, which is ascribed to the metal and oxygen together. *Metallic iron* has long been used for purifying water, as in Anderson's process (J. Soc. Arts. Feb. 14, 1896) ; in this case, galvanic action and the oxides formed come largely into play, but Frankland proved that the metal itself was, to a certain extent, bactericidal. Old Hindoo writings direct water to be kept in vessels of *copper* ; among modern observers,

Nageli, Galeotti, and Israel and Klingman hold that there is formed a colloidal solution which renders the water toxic to many algæ and bacteria. In 1904 the U.S. Dept. of Agriculture reported that 1 sq. cm. of bright copper per 100 c.c. of water was sufficient to exterminate *Uroglena* and some forms of *Spirogyra*, and Kraemer showed that the same treatment destroyed colon and typhoid bacilli in 4 hours, whilst colloidal copper was quickly fatal to these organisms. For household purification, he commended the use of strips of copper, about $3\frac{1}{2}$ sq. inch to each quart (2 sq. cm. to 100 c.c.), immersed in the water for 6 to 8 hours. In a similar way, Rideal and Baines (J. San. Inst. 1904, 594) obtained sterilisation of *typhosus*, *coli*, and *S. py. aureus* in less than 24 hours. Bassett Smith (J. Prev. Med. July, 1904) found that in a bright copper vessel, *B. typhosus* was still living at 12 hours, but was dead at 24, and that of ordinary water organisms, 1020 per c.c. at first, only 8 per c.c (none of them liquefying) were left after 24 hours He concluded that clean iron or zinc was nearly equal to copper in first effect, but soon lost the power by oxidation.

Copper salts have a distinctly poisonous action on lower organisms, and are now used in many places to retard algæ development early in their seasonal growth in water reservoirs. Kroncke considered *cuprous chloride* to be the most active of the salts : he treated Elbe water, containing 40 to 50 thousand organisms per c.c., with 50 parts per million of Cu_2Cl_2 and 20 parts of ferrous sulphate, allowed 6 hours' contact, then agitated with 10 parts of lime. After settling and filtration through sand, the water was sterilised, clear, and colourless, and free from iron and copper. Schumberg (Chem. Zentr. 1900, ii. 203) corroborated the sterility at the end of 6 hours. The efficiency of soluble cupric salts is generally dependent on their percentage of copper (Green, Zeitsch. f. Hyg. 1893, 495 ; Rideal and Baines, l.c.), but the sulphate is commonly used as most convenient. For disinfecting sewage effluents (and inferentially for reservoirs), American investigations conclude that copper sulphate 'is not so efficient as chlorine compounds, is more seriously affected by carbonates, and is much more expensive' (U.S. Geol. Survey, Water Supply Paper 229, 1909, 32 ; also see Bull. U.S. Dept. of Agric. No. 100, 1906).

Disinfection of excreta and morbid products, even with considerable quantities of copper salts (e.g. 5 to 10 p.c. of the sulphate), is not reliable. For killing agricultural parasites, their use is well known, including that of the sulphate for soaking seeds and against potato blight, also verdigris (acetate), 'Paris green' (arsenite), copper-lime-sugar and copper-soap washes for trees, and 'Bordeaux mixture' (copper sulphate and lime). The last named was introduced in the former way, but has been since extended to other crops. In reference to the general practice of employing the metallic compound in the precipitated or solid form, instead of in solution, the main points stated are (1) that, in the former way, it is not liable to injure the plant or contaminate its tissues ; (2) that the copper should remain as an external coating, because the spores germinate on the surface ; (3) that uncertainty of composition

and inequality of application are overcome by certain precautions and definite prescriptions. See British Board of Agriculture leaflets 23 and 225 ; the latter (May, 1909) gives a method of preparing and using Bordeaux mixture : 'for a 3 p.c. solution, 3 lb. copper sulphate and 2 lb. freshly burnt quicklime to 10 gallons of water.' See also J. Soc. Chem. Ind. 1896, 332 ; 1907, 1291 ; Compt. rend. 1911, 152, 532. Chuard (ibid. 1910, 150, 839), estimating that 12,000 tons of copper are thus consumed annually in France, expresses anxiety as to the result of its accumulation in the surface soil, and with a view to reducing the quantity states that a half p.c. aqueous mixture of the oxychloride is as adhesive and effective as the usual 2 p.c. paste of the sulphate. Cupric sulphate impregnation for preserving or 'kyanising' timber has been superseded by creosote oils, since the former washed out of the wood. 'Microsol,' sold as a soluble disinfectant for stables and drains, contained 75 p.c. of copper sulphate with sulphocarbolate and some free sulphur dioxide.

Mercury.—Mercuric chloride, 'corrosive sublimate,' has long been recognised as one of the most powerful of disinfectants, and a 1 per 1000 solution was the earliest standard for comparisons. Apart from cost, points limiting its utility to special purposes are : (1) the poisonous effect on higher animals and plants ; (2) its precipitation by so large a number of substances, such as hard water, alkalis, and numerous salts, metals, sulphides, and many organic bodies, causing its action to be liable to great variations and inconveniences. It will often form a pellicle over organisms without killing them, and it is inapplicable to the disinfection of sputum, excreta, and the like, from its producing a coagulum which prevents further penetration. Sodium or ammonium chloride is sometimes added to increase the stability of the aqueous solution, but considerably diminishes the germicidal power. The Local Government Board recommended for disinfecting purposes : $HgCl_2 \frac{1}{2}$ oz., HCl 1 fluid oz., aniline blue 5 grs. (a colouring for safety), water 3 gallons (1 in 962).

Kronig and Paul in 1897 showed that mercury salts followed a general rule that the germicidal power depends on the metallic ion, and is in proportion to the degree of ionisation, so that a 1 in 500 solution of $HgCl_2$ is much less than twice as active as 1 in 1000 : moreover, the chloride is more active (in equivalent solutions) than the bromide, and 4 times more active than the cyanide, which is almost non-ionised. Solutions of the *oxycyanide* are used in surgery, are distinctly *alkaline*, and only slightly precipitate albumen ; a strength of 1 in 1500 is antiseptic, does not really attack instruments, and is not irritant. *Mercuric iodide*, dissolved in potassium iodide, is a powerful disinfectant, and is made up as 'iodic hydrarg.' It is less affected by albuminoids and less irritant than the chloride, and is incorporated in a disinfectant soap. *Mercury-zinc cyanide*, 'Lister's antiseptic,' has the disadvantage of being of variable composition. A great number of organic mercurial compounds, introduced into medicine and surgery, trace their main effect to an antiseptic or germicidal action. '$Sublamin,$' mercuric-ethylenediamine sulphate (43 p.c. Hg), is easily

soluble in water, is much less irritant than mercuric chloride, does not coagulate albuminous solutions nor precipitate soap, and is a valuable hand-disinfectant. 'Proteotyl' contains about 96 p.c. water, 1 p.c. salicylic acid, 0·2 p.c. mercury, and about 3 p.c. gelatin.

Sodium hydriodic mercurobenzoate was carefully investigated as a disinfectant by Schroller and Schranth (Zeitsch. f. Hyg. u. Infect. Kranh. 1911). They found that the germicidal powers could be enhanced by the introduction of halogens, methyl, methoid, or a second hydroidic mercury group into the nucleus, whilst a corresponding depression was caused by sulphonation or the introduction of an amino grouping, sodium oxymercury ortho-nitrophenolate. 'Mercurophen' is said to have a carbolic acid coefficient by the R.W. method of over 10,000, to be less toxic than mercuric chloride, and to exert less than one-quarter of the precipitating power which this salt has on blood serum (S. Schamberg, J. Amer. Med. Assoc. 1917).

Silver nitrate stands next to mercuric chloride in germicidal power, and has similar limitations in its use, with the additional one of being precipitated by chlorides. The writer found that 1 in 1000 killed *B. coli* and *S. py. aureus* in 24 hours, but a small quantity of chloride or organic matter prevented the effect. Among other silver salts are the citrate, 'Itrol,' recommended as a non-irritant antiseptic dusting for wounds (Pharm. Zentr. 38, 460); 'Actol,' the lactate, for antiseptic injections: 'Tachiol' silver fluoride, easily soluble, and a powerful non-toxic bactericide specially useful for the urinary tract (1 in 1000 to 1 in 5000 is suggested by Paterno and Cigolani for sterilising water in a concentration of 1 in 400,000. Chiefly with the object of avoiding irritant action, incompatibility with chlorides, and coagulation of albuminoids, a large number of organic preparations of silver have been introduced, such as 'argentamino' (ethylenediamine-silver-phosphate), and the proteid compounds 'argonine' (casein), 'argyrol' (gluten), 'largin' (albumen), and 'protargol' (protein). A report to the British Med. Assoc. in 1906 gives the time in minutes required to kill *S. py. aureus* by the preparations used as: silver nitrate (½ to 2 p.c.), 2 to 5; protargol (2 to 4 p.c.), 3 to 5; largin (10 p.c.), 2 to 5; argonine (5 p.c.), 3 to 6; whilst argyrol and 'collargol' (colloidal silver, J. Soc. Chem. Ind. 1903, 315) had very little bactericidal power (Lancet, 1907, i. 675). Many of these are destructive to gonococci and to ophthalmic disease organisms.

Osmic acid was found by Koch and Kleih to be powerfully bactericidal; it is very poisonous and a strong oxidiser. The former stated that an extremely dilute solution of *potassium auricyanide*, 1 part $Au(CN)_3$ in 2 millions, checked the growth of *B. tuberculosis*.

Chick and Martin (J. of Hyg. 1908, 634) observe that for spores, metallic salts rank highest as germicides; with mercuric chloride, the reduction of efficiency caused by blood srum is much greater than with phenol.

ORGANIC COMPOUNDS.

Compounds related to the alcohols. It has long been known that 'wood spirit,' crude

methyl alcohol, in a dilution as low as about 5 p.c., can kill insects and most micro-organisms, and preserve perishable organic materials owing to the tar products that it naturally contains. The alcohols, by themselves, are only efficient in a very much higher strength by coagulating albumen and (when absolute) by withdrawing water. Wirgin (Zeitsch. Hyg. 1904, 46, 149) has tested methyl, ethyl, butyl, and amyl alcohols with anthrax spores, and *S. py. aureus*, and concludes that the disinfecting power is low, that it increases with the molecular weight, and that there is scarcely any action on dry spores. It has been suggested to add alcohol vapour in steam disinfection, but Seige (Chem. Zentr. 1902, 1, 130) finds no advantage. Hand-disinfection with alcohol is not reliable (Goenner; Harrington, Boston M. J. May 21, 1903), although Hansen found that epidermal bacteria, *e.q.* eczema, are, when moist, destroyed in one minute by absolute, and in most cases by 50-60 p.c. alcohol (Centr. Bakt. 1907, 466). This statement is supported by A. Zabludowski (Deut. Med. Wochenschrift, 1911, 405), who advised the addition of 5 p.c. of tannic acid. Sterility of the hands could be obtained by 2 minutes' immersion. *Glycerol* in strong solutions (25 p.c. and upwards), is antiseptic, but in weaker ones it rather promotes the growth of bacteria. *Allyl isothiocyanate*, mustard oil, has figured in a number of patents, and is capable of killing many organisms, but not economically.

Formaldehyde is found in commerce as the 40 p.c. solution 'formalin' or 'formol'; it is antiseptic and germicidal, and is official in the German, Austrian, Belgian, United States, and Japanese pharmacopœias. Formalin, diluted 10 times, is used for embalming and for preserving bodies for dissection and museum specimens, but for antisepsis generally, a much weaker solution is efficient. The Board of Agriculture (Dec. 1906) found that fruit of all kinds immersed for 10 minutes in a solution of 3 pints formalin to 10 gallons water (=1¼ p.c. CH_2O), then allowed to drain and dry, keeps 10 to 21 days longer than when untreated; and that one lot of liquid can be used for a number of batches. S. Rideal and Dr. Foulerton have proved that 1 in 50,000 of formaldehyde (=1 in 20,000 of formalin) suffices to keep milk sweet for 24 hours, even in warm weather, without injury to health (Pub. Health, May, 1899; Lancet, 1899, 1427, 1571). Apparently because experiments with larger doses showed effects on nutrition, the British Dept. Committee on Preservatives, in 1901, recommended 'that the use of formaldehyde or formalin or preparations thereof in foods or drinks be absolutely prohibited.' And yet its agency in the preservation of food is as ancient as that of salt. The disinfectant and preservative power of wood-smoke is in part due to formaldehyde, which is present on the surface of smoked provisions,[1] and was found by Trillat in amounts varying from $\frac{1}{10000}$ to $\frac{1}{100000}$ of the weight of the substance consumed, in smoke from wood and cellulose. In tobacco smoke, he found 0·05 to 0·12 p.c., and in soot from house chimneys, 0·28 to 0·35 p.c.

[1] Petrier finds $\frac{1}{10000}$ to $\frac{1}{100000}$ in bacon, ham, sausages, and herrings; remarks that a strict regulation against formaldehyde would forbid these foods; and contends that a limit should be fixed instead of prohibition.

as paraformaldehyde. Typhoid and cholera organisms were killed by products from the combustion of 2 grams of sugar passed into a 12 litre vessel, and by burning 4 kilos. of sugar in a room of 100 cub. metres ' even very resistant organisms were destroyed.' (Rouguier has made this the basis of Fr. Pat. 360476, 1905.) With straw, the best results were obtained by burning it in a heap of alternate dry and wet layers : using 18 kilos. of straw in a room of 140 cub. metres (4944 cub. feet), *B. coli* and *diphtheriæ* were destroyed after contact with the smoke for 12 hours ; the room temperature rose to 35°, and up to 2 grams of formaldehyde were generated per kilo. of straw (Compt. rend. 138, 1613 ; 139, 742 ; 140, 797 ; 141, 215 ; 150, 339).

H. Will (Zeitsch. Brauw. 1905, 28, 330, 347) gives formalin a very high place among brewery disinfectants. He notices, like other observers (Kingzett, Slater and Rideal, Lancet, April 21, 1894), that it is more powerful against bacteria than against yeasts and mould fungi. Limits recorded as preventing development are : sarcinæ and bacteria, 0·003 to 0·031 p.c ; yeasts, 0·007 to 0·062 p.c. ; moulds, 0·031 to 0·125 p.c.

Advantages in formaldehyde disinfection are : (1) that it can be easily applied in the state of gas or vapour for fumigation ; in the liquid condition as spray, wash, dipping, or in higher dilutions as an antiseptic, or in the solid form as its polymers, compounds, or mixtures ; (2) that unlike mercuric chloride and many other agents, it is not thrown out of action by albuminous matter or by most chemicals ; (3) that it is effective in strengths which are not irritant or poisonous, and does not injure fabrics or metals. At quarantine stations, large quantities of bulbs, roots, nuts, fruits, &c., coming from plague or cholera-infected regions are disinfected by immersion in a 5 p.c. solution of formalin, which does not injure the food value and much retards decay. In the Linley process, meat is treated with formaldehyde vapour, ' 1 oz. formalin per cub. foot of space in the chamber,' the gas after a time removed by a fan, and the meat frozen for shipment. Buchanan and Schryver (L.G.B. Food Report, No. 9) state that the gas commonly penetrates for about 20 mm. under a thin layer of connective tissue, that the amount absorbed often reaches 1 in 3500, that it is reduced or removed by boiling or roasting, but that grilling seems to make it penetrate further.

In surgery, formaldehyde and its preparations have been of wide service. Amongst the more important may be mentioned the following formaldehyde and formaldehyde ammonia (hexamethylene tetramine) compounds :—

	With formaldehyde	With hexamethylene tetramine
Inorganic compounds	Glyceroborate or boroform	Triborate or borovertin
	Aluminium silicate or dreiaform	Dichromate or chromoform
		Acid phosphate or hexanitrine
Aliphatic derivatives	Iodoform or eteaiodoform	Dibromodiiodo chrysoform
	Acetamide or formicin	Sodium acetate or cystopurin
		Iodoform iodoformin

	With formaldehyde	With hexamethylene tetramine
Aromatic derivatives	Phenol Resorcinol Guaiacol Thymol Cresols and potash or tysoform Tar and pitch	Resorcinol Guaiacol Salicylates Salicyl-sulphonates
Carbohydrates	Lactose Dextrin Milk sugars	Milk sugar
Miscellaneous	Starches Casein Gelatin Terpenes Tannins	Silver albumin Camphorate Tannins

Geronzi found that the addition of 5 p.c. of sodium carbonate to the 5 p.c. formalin which he successfully used for obstinate ear disease increased the tolerance and enhanced the germicidal power (Arch. Ital. di Otologia, 1903).

Formaldehyde antiseptic powders for dressing are ' Amyloform ' (starch) ; ' Proteol ' (casein) ; ' Steriform ' and ' Sterisol ' (lactose) ; ' Glutol ' (gelatin). These, especially the last, when moistened as in a wound, slowly regenerate formaldehyde. Formalised gelatine is now largely used with success instead of surgical collodions. *Formamint tablets*, ' for infectious diseases and as a prophylactic,' are said to contain 0·01 gram of CH_2O in each, combined with milk sugar (Eng. Pat. 2672, 1906 ; Pharm. J. 1907, ii 838). M. Jones states that with *B. diphtheriæ* the R.W. coefficient is only 0·01 as against 0·30 for cyllin pastiles.

Paraform, paraformaldehyde, trioxymethylene, or ' triformal,' is a solid polymer, only slightly soluble in cold water, and dissociated into CH_2O gas on heating. It was introduced as an internal antiseptic and for disinfecting instruments, and said to be as active as β-naphthol, but its chief use is for evolving formaldehyde either alone or in mixture, for which a large number of methods have been proposed, many of them patented. Mixtures with Na, Ba, or Sr peroxide, when brought into contact with water, yield formaldehyde and hydrogen peroxide : it is stated that ' Autan ' contains 1 part of paraform to 2 of BaO_2 (Lancet, 1908, i. 139), and that 50 grams mixed with water kills all organisms in a cubic metre of air bubbled through it (Fr. Pat. 366605, 1906).

Room disinfection with formaldehyde cannot be economically effected by simply evaporating the solution ; under ordinary circumstances, only a portion of the substance is volatilised, the remainder polymerising and remaining behind as a solid, while reliable disinfection requires a definite large volume of gas to be produced in a short time. For this object, very numerous methods and apparatus have been devised, which may be grouped as follows:—

A. Direct production of CH_2O gas, by passing methyl alcohol vapour and air over hot surfaces of platinum (Hofmann) or partly oxidised copper (Loew). The various lamps on this principle have had the faults, among others, that the oxidation is incomplete and inconstant. Kenwood found that 1½ litres of methyl alcohol were required to disinfect a room of 2000 cub. feet.

B. Heating the solution (formalin) under pressure was used by Trillat, calcium chloride being added to raise the boiling-point. In his *autoclave*, 1 lb formalin was required for 1500 cub. feet. By this method, Kenwood obtained sterilisation of diphtheria swabs, and S. Rideal with various articles infected with *B. typhosus*, *diphtheriæ, coli*, *S. py. aureus*, and anthrax spores, found that in 24 hours all were sterilised, whilst fabrics, furniture, metals, and leather were not injured. (*See also* J. R. San Inst 1903, 508.)

C. Formalin, mixed with glycerol, is distilled at nearly the ordinary pressure, as in the Trenner-Lee, Lentz, and Lingner apparatus. The latter, according to the Russian National Health Society's Journ. 1900, was mainly instrumental in extinguishing the plague at Astrachan, in 1899. Klein (report of 1902), by 3 hours' exposure in a sealed room with the Lingner generator, sterilised anthrax spores and tubercular sputum. Houston and Newman also report favourably (Practitioner, Sept. 1902)

An important point to notice is that in method (B), the CH_2O is chiefly liberated at the beginning of the operation, in (C) at the end, mixed in the latter case with steam and glycerol spray, which deposits as a film on the surfaces, and assists in the penetration and disinfectant action.

D. Formaldehyde has also been used in conjunction with acetone (Eng. Pat. 10398, 1908), SO_2 (Fr. Pat. 379998, 1906), alcohol, and some fatty acids.

E. Evolution by mixing with other chemicals. Dehydrating agents disengage very little CH_2O gas from formalin, since most of it polymerises. With quicklime, S. Rideal has only obtained 8 p.c. of the theoretical yield (*cf.* Eng. Pat. 8259, 1899; Fr. Pat. 323041, 1902; and U.S. Pat. 790468, 1905). Carteret observes (Compt. rend. 1908, 146, 819) that 1 part formaldehyde and 2 parts bleaching powder added to 3 parts water evolve 70 p.c. of the theoretical yield (D. R. P. 217204 of 1908). Potassium permanganate behaves similarly, generating great heat; U.S. Pat. 885223 relates to a mixture of this kind. Major Munson (Trans. Inter. Congress Hygiene, Washington, 1913, 756) has obtained 86 p.c. of the formalin vaporised, and S. Rideal (Blackpool Congress, 1914) used a paper bag for sterilising clothes, using 40 grams permanganate to 100 c.c. formalin. The action of peroxides has been already mentioned.

F. The simplest process is heating paraform by a small flame (avoiding ignition), when it melts and is resolved into CH_2O. The 'Alformant,' or Schering lamp, uses 1-gram tablets placed in a perforated cup, and it is directed to use 10 tablets per 1000 cub. feet with 6 hours' exposure. S. Rideal found that this quantity killed *B. coli, typhosus, diphtheriæ*, and *S. py. aureus* in 20-24 hours, and that double the quantity in the same time killed *moist*, but not always *dry* anthrax spores. He recommended spraying with $\frac{1}{2}$ p.c. solution of formalin before using the lamp, as the gas is evolved with insufficient moisture. The latter defect is remedied in the 'hydroformant' lamp, in which 12 ozs. of water in an annular vessel is simultaneously evaporated. Rosenau considers this method of generating CH_2O useful for the disinfection of closets and small enclosures of

less than 100 cub. feet, with not less than 12 and preferably 24 hours' exposure, and not less than 2 ozs. of paraform per 100 cub. feet (about 2 grams per cub. metre). Klein, Houston, and Gordon (London County Council, 1902) record that with 23 grams of paraform per 1000 cub. feet, *B. typhosus, diphtheriæ, pyocyaneus*, and *S. py. aureus* were killed in 5 hours, but not anthrax spores nor (with certainty) *tuberculosis* in sputum. It will be noticed that the time is not even that given in the directions issued with the lamp, and the humidity and temperature of the room are not stated. Allan, Newman, and Cribb had previously obtained generally satisfactory results with 10 grams paraform per 1000 cub. feet, under moist conditions (Brit. Med. J. Aug. 13, 1898). Kenwood's experiments pointed to an average of 25 grams per 1000 cub. feet being necessary. Werner and Bonhoff (Berl. Klin. Woch. 1904) find that tubercular sputum is certainly disinfected by 5 grams per cub. metre (141 grams per 1000 cub. feet) acting for 7 hours, which is double the quantity Flugge first recommended. In Breslau a large number of formaldehyde disinfections are carried out for scarlet fever and measles, and the disease has in no case recurred in the same room.

Spraying with the solution should be the invariable practice except with the large CH_2O generators, which are capable of filling the room also with steam and spray. When spraying is used alone, there is a danger of not penetrating into crevices, and the solution must be of higher strength; Dr Mackenzie's extensive experience in the disinfection of houses and hospital wards, proved that 1 p.c. CH_2O (4 ozs. formalin per gallon) is attended with success; he adds 5 ozs. glycerol per gallon of formalin to prevent too-rapid drying. Thresh and Sowden in 3 to 4 hours sterilised *diphtheria, typhosus, cholera, pyoq. aureus*, and *prodigiosus* with $\frac{1}{2}$ p.c. CH_2O, but *pyocyaneus* (on whitewash) only with 2 p.c.; they, therefore, recommend the latter strength.

Where the space has to be occupied soon afterwards, any residual formaldehyde can be neutralised by volatilising ammonia. The product, under the name of *Urotropine*, is a serviceable antiseptic in cystic affections, and is administered to typhoid 'carriers' to destroy the bacilli of the disease in the urine. Urotropine is the basis of a large number of antiseptic preparations (*see* above).

Disinfection of excreta is attained by mixing with 3 to 5 p.c. of formalin and keeping in a closed vessel for at least an hour. Rosenau states that faeces are rendered sterile at the end of 10 minutes by an equal volume of a 4 p.c. solution of formalin. Houston prescribes 1 to 2 pints (according to bulk) of 5 p.c. formalin, acting for at least an hour (Practitioner, Sept. 1902).

Formaldehyde, as an insecticide, is much inferior to SO_2, although Brough (J. Mass. B. of H. March, 1898, 51) observed, in his disinfections with the former gas, that all the flies were invariably killed, and generally the bed-bugs. It is an excellent deodorant.

No acidity is produced by continuous spraying or distillation of formaldehyde, therefore it is not readily converted into formic acid in this way.

Formic acid.—We have discussed the germi-cidal action of acids generally in an earlier section of this article. Formic acid has this power to a considerable extent, and is a strong antiseptic. Kitasato's results, as summarised by Horrocks, gave acetic acid a slightly higher activity in nutrient media, stating that with *B. typhosus* the amounts p.c. in cases of (1) growth, (2) growth restrained, (3) no growth, were respectively : formic acid, 0·22, 0 278, and 0·356 ; acetic acid, 0·2, 0·225, and 0 3 ; with *Sp. choleræ*, formic, 0·11, 0 167, 0·22 ; acetic, 0·1, 0·153, 0·2. But very different results are ob-tained in water and most organic solutions The writer has found that *typhosus* is killed by 0 5 p.c. of formic acid in less than 15 minutes, and by 0·1 p.c. in about 30 minutes ; and in 1907 he made the R.W. typhosus coefficient of formic acid many times higher than that of acetic. He also found the preservative action to be higher : with vegetable substances, 1 p.c. of formic acid was equal in effect to 5 p.c. of acetic (time of trial, 2 months). Raw fish were mounted in 0·53 p.c. formic, in 5 p.c. acetic, and in 0 3 p c boric, acids, heated for 20 minutes to 80°, and the jar closed with cotton wool ; in a week, the last was brownish, disintegrated, and uneatable, though not distinctly putrid ; while the first two kept sweet and of natural characters for 3 months. Experiments with bread-pulp infected with a mixed mould-growth proved that 0 1 p.c. of formic acid entirely inhibits the growth for several days, even under the most favour-able conditions of culture. But in the de-struction of the spores, formic acid is less effective than formaldehyde. Lebbin (Chem. Zeit. 1906, 30, 1009) effectively preserved different classes of foods by 0 15 p c of formic acid, and others have proved that in the quan-tities mentioned above it is physiologically harmless ; the taste is more pleasant than acetic acid, and the odour is not noticeable. B. H. Smith (J. Amer. Chem. Soc 1907, 1236) preserved vegetables with formic, with salicylic and with benzoic acid, in unprotected jars. Under conditions in which the untreated samples became sour and mouldy in 2 days, 0·1 p c. formic acid preserved them for 7 days, 0·3 p.c. for 12 to 18 days, 0·5 p.c. for 25 days, 0 7 p.c and 1 p.c. for 45 to over 85 days, and 2 p c. for over 85 days. He states that 0·1 p c of benzoic acid kept his sample for 85 days, whilst with the same quantity of salicylic acid it was sour in 9 days. In ordinary preserving practice, as we have seen, the articles would have remained good for the longer time with the smaller quan-tities of formic acid, which, even if it must be applied in a somewhat higher proportion, is from physiological and physical reasons pre-ferable to salicylic or benzoic. The chief formic acid preservatives used in commerce, mainly for fruit preparations, are 'Werderol' and 'Fructol' (10–14 p.c. formic acid, '1–1½ p.c. of the liquid to be added'); and 'Alacet' (made synthetically from CO and NaOH at the Nitritfabrik, Köpenick, about 50 to 60 p.c. formic acid, 'use 0·3 p.c. of the liquid'). The result in the three cases would be about 0·14–0·18 p.c. of the acid. In an investigation of these articles by Croner and Seligmann (Zeitsch. f. Hyg. 1907, 56, 387), they find that inhibition of moulds, yeasts, and acid-forming organisms

begins at 0·15 p.c. formic acid, that sterilisation is effected in 24 hours by 0·2 p.c., and in 10 to 30 minutes by 1 p.c.

Only the free acid is active against organisms, although the salts do not favour the growths as do the alkaline acetates. Sodium formate helps the solubility of many antiseptics without lessening their power, therefore figures as an adjunct in a number of patents.

Acetic acid is one of the most anciently used of preservatives ; 'aromatic vinegar,' a more or less concentrated acid containing essential oils, had a partially-justified reputation against in-fection. The writers find that *B. coli* is killed by 5 p.c. HA in 5 minutes, by 2·5 p.c. in 15 minutes, while with 0·5 and 0·1 p.c. it is alive after 40 minutes. *Pyroligneous acid*, or crude wood vinegar, owes its antiseptic power chiefly to the presence of creosote and formaldehyde.

Acetyl peroxide and benzoyl-acetyl peroxide are stated by Freer and Novy (Amer. Chem. J. 1902, 27, [3] 161) to be strongly germicidal, since solutions corresponding to 0·037–0 074 p.c. of the former, or 0 056–0·112 p.c. of the latter, =0·005–0·01 p.c. of active oxygen, destroyed within a minute all known disease-producing bacteria, and even spores of *B. mesentericus*, which are not killed by 5 p.c. phenol ; whilst H_2O_2 solution containing 0·05 p.c. of active O was without action on many bacteria even in 60 minutes. Benzoyl peroxide had no oxidising action, and was without effect on bacteria. A solution of acetyl peroxide was introduced under the name 'acetozone,' but the title is now applied to a more convenient and stable mixture of the benzoyl-acetyl compound with infusorial earth, said to be useful in typhoid, dysentery, and cholera (Lancet, 1904, ii. 1160 ; Brit. Med. J. 1907, i. 634).

Propionic acid has been tested comparatively by Duggan (Amer. Chem. J. 7, 62) with the highly resistant *B subtilis*. He gives as the strengths necessary for killing : formic acid, 7 p.c. ; acetic acid, 9 p c. ; propionic acid, 12 p c. (numbers proportional to the molecular weights). According to A. C. Jordan (Prac-titioner, Sept. 1902, 297), 0·1 p c. of *butyric acid* in broth tubes infected with vigorous *B. coli* or *typhosus* caused them to remain sterile ; *S. pyog. aureus* required 0 2 p c. *Valeric acid* is a feeble antiseptic, but has been introduced along with a little creosote, as an internal antiseptic called 'geosote.'

Oleic acid, the fats, 'Lanolin,' &c., have but slight antiseptic power in themselves, but when applied to the skin may prevent infection by the exclusion of germs. Reichenbach (Zeitsch. f. Hyg. u. Infect. 1908, 59, 296) showed that the alkali salts of the palmitates had the strongest bactericidal action of the soaps investigated. The potassium salts of the saturated fatty acids are comparatively strong bactericides, but those of the unsaturated acids, with the exception of elaidic, are not. Vicario, however, observed that the fatty matters some-times already contain germs, and Baldas (Giorn. R S. Ital. d' Igiene, Feb. 1901) proved that *B. coli* and *typhosus*, *S. pyog. aureus* and *albus*, retained their virulence in oils for 2 months ; therefore ointment bases require to be sterilised by heating to 100°, or preferably to 120°, as various bacilli survive in oil far

longer than in aqueous solution. In fatty media antiseptics and disinfectants, as a rule, are much less active than in water, hence the ineffectiveness of carbolised oil as shown by Koch and Breslauer. Lanoline and cold cream contain water, so can enable agents in aqueous solution to come in contact with micro-organisms Some metallic oleates are parasiticide : cupric oleate in ringworm and favus (Lancet, 1907, i. 510) ; mercuric oleate for pediculi ; zinc oleate is said to cure chronic eczema.

Vegetable acids have the general power of inhibiting bacteria which prefer a neutral to an acid medium, but their effect is much less than that of mineral acids, and their solutions quickly become mouldy in warm weather. Citric acid was formerly recommended for sterilising water : Dr. Christmas in 1892 stated that cholera organisms were killed by 0·08 p.c. and typhoid by 0·10 p.c. Kitasato's figures for tartaric, citric, and malic acids added to neutral media containing *typhosus* are in p.c.'s : growth, 0·338 ; growth restrained, 0·384 ; no growth, 0·476. Succinic acid is slightly antiseptic. ' Alphogen ' or ' Alphozone,' succinyl peroxide, is said to be a powerful germicide (Lancet, 1905, i. 367).

Aromatic acids.—The introduction of —COOH groups or aliphatic acid radicals into the benzene ring yields acids of relatively low antiseptic power, increasing with the molecular weight of the entering acid.

Benzoic acid is strongly antiseptic in solution and vapour, and to a rather less degree in its soluble salts. It dissolves in about 400 parts of cold water, and the saturated solution kills *B. typhosus* in a few minutes. When molecular proportions, *i.e.* sodium benzoate 0·026 p.c., potassium benzoate 0·029 p.c., benzoic acid 0·022 p.c., are separately mixed with milk, the writer observes that all retard the souring, the acid more than its salts, but the effect comes to an end sooner than with inorganic salts like the fluorides, since benzoic acid is itself decomposed by some organisms (Analyst, 1907, 32). Not being poisonous, it has been much used as a food preservative, particularly in countries where salicylic acid was forbidden. Following a report of the Referee Board of the U.S. Board of Agric. that doses of benzoates under 0·5 gram per day were not injurious to health, and that even 4 grams per day did not act as a poison, the U.S. Board, in Pamphlet 104, 1909, have announced that they will make no objection to the use of sodium benzoate in food, provided it is plainly labelled on each package, both as to presence and quantity. The taste and odour are difficult to mask. It has long been used as an antiseptic in surgery, *e.g.* in ' Friar's Balsam ' (tinct. benzoini co). *Benzoic aldehyde* is official in the U.S. Pharmacopœia, and in the form of commercial oil of bitter almonds owes its parasiticide power in ointments mainly to the hydrocyanic acid it contains, which, of course, necessitates care in use. *Benzoyl-sulphonic-imide*, ' Saccharin ', or ' Gluside,' has some preservative power, and has been given internally to stop decomposition of urine in cystitis, but its use for sweetening is less on account of this power than because it is itself unfermentable.

Salicylic acid.—The saturated aqueous solu-

tion contains 1 in 500 : tested with *typhosus*, *pyog.*, *aureus*, and *anthrax*, Westcott found that in 3 hours only the former was killed. As a food preservative, it is about equal to benzoic, their relative activities varying under different circumstances. Its physiological effect is more distinct than that of boric or formic acid or formaldehyde in the small quantities required, but there is no clear evidence that it causes injury to adults if the amount is limited. The British Depart. Committee's suggested restriction is that it ' be not used in a greater proportion than 1 grain per pint in liquid food and 1 grain per lb. in solid food,' or 0·0114 and 0·014 p.c. respectively, which practically would amount to a prohibition, since moulds and ferments are only reliably inhibited by 0·1 p.c., the amount commonly employed, though often exceeded. Addition of the acid to foods is forbidden in France, Austria, and some other countries. Traces are present in a large number of fruits (Analyst, 1903, 149). Dr. Linga G. Anderson used extensively a saline gelatined salicylic acid paste containing 2 p c of the acid as a wound dressing with satisfactory results. Compounded with an equal weight of boric acid it is also used as a first dressing under the name of Borsul. ' Salol ' is phenyl salicylate, an internal antiseptic which is decomposed in the duodenum into phenol and salicylic acid. According to Lowenthal, when mixed with pancreatic juice, it rapidly kills *Sp. choleræ* (Compt. rend. 107, 1169). ' Salophen,' *p*-aminophenyl acetyl salicylate, is said to have a rather stronger antiseptic power (Practitioner, March, 1907). A large number of derivatives of salicylic acid have been introduced, and many of them patented.

Cinnamic acid, at 2 p.c., prevents the growth of bacteria, and at 4 p.c. destroys them. It is contained in Peru and storax balsams, which are parasiticide in skin diseases. Fr. Pat. 371091 preserves butter by enclosing it in a wrapper impregnated with cinnamic acid, which ' prevents butyric fermentation.' *Acetyl-o-coumaric acid*, ' Tylmarin,' is another internal antiseptic, said to have a R.W. coefficient of 4·5. The use of halogen substituted hydrosic acids, especially 6-chlor-3-hydroxy-*p*-toluic acid, has been suggested for disinfectant purposes (J. Soc. Chem. Ind. 1914, 33, 807).

Tannin is antiseptic to proteids through its property of forming with them insoluble compounds such as leather, but none of the tannin extracts have even the power to preserve their own solutions.

Phenols and phenoloids. The introduction of aliphatic side chains into the nucleus of phenol raises the germicidal activity ; the *o-* and *p-* positions for the entering groups have a greater influence than the *m*. Morgan and Cooper found the following C.A. coefficients for three cresols, *o*=2·1, *p*=2·4, *m*=2·0. Whilst trimethol trimethyl methoxy phenol is said to have a R.W. coefficient of 40 when properly emulsified.

For general purposes of disinfection, ' coaltar ' fluids, having as their chief active constituents bodies allied to phenols, are most extensively employed. They are usually dark syrupy liquids smelling of coal tar, and may be roughly divided into two classes : (1) those

which on the addition of water form a more or less clear dilution; and (2) preparations miscible with water but producing an emulsion. The former usually consist of saponified tar-acids: the *liquor cresoli saponatus*, Ph. G., consisting of equal parts of potash soap and crude cresol heated together, is of this nature. In the manufacture of these fluids, potash soap, glycerol, alcohol, and other agents are employed to aid the solubility in water. With the second group, the mostly insoluble, active ingredients are emulsified by the aid of soda, soaps, resin, neutral oils, or gelatin.

Polyhydric phenols and naphthols. The antiseptic powers of the di- and trihydroxybenzenes are less than those of phenol.

Resorcinol, m-dihydroxybenzene, is a powerful medicinal antiseptic, and a 1 p.c. solution kills most organisms. Andeer's lotion' contains 40 grains in 1 oz. water. 'Anusol' is a bismuth iodo-resorcin sulphonate. *Quinol* or hydroquinone, *p*-dihydroxybenzene, is said to be a stronger antiseptic than the last, and has been suggested for typhoid in doses of 3 to 8 grains. The ortho- compound, *catechol* or pyrocatechin, is also antiseptic. Duggan finds (Amer. Chem. J. 7, 62) that the amounts of the three isomerides required for preventing development of *B. subtilis* in broth are: ortho- 20, meta- 25, para- 30; phenol being 20 and pyrogallol 15. Morgan and Cooper (8th Int. Cong. App. Chem. 1912, viii. cl.) give the following figures for the carbolic acid coefficients: ortho- =0·48, meta- =0·29, para- =1·1.

Pyrogallol, tri-hydroxybenzene, is antiseptic, and a 3 p.c. solution kills most bacteria, particularly aerobes, but it stains, is unstable, and very poisonous.

Guaiacol (methyl-catechol) and *creosol* (methyl-guaiacol) are the active ingredients in wood creosotes, and have been widely useful as antiseptics and parasiticides, especially in tuberculosis. Guaiacol has an antiseptic power (but not bactericidal—*see* Table) 2½ times that of phenol, and a ½ to 1 p.c. solution destroys *B. tuberculosis* in 2 hours (Marfori, Ann. di Chim. 12, 3). A one in 150 solution of (Morson's) creosote kills *pyog. aureus* and *typhosus* in 3 hours (Westcott). 'Little's Soluble Phenyle' contains wood creosote, and Corfield's experiments give it a high value for wounds and against vermin. Kenwood and Hewlett (J. R. San. Inst. 1906, 13) make its R.W. coefficient 1·2.

Beta-naphthol is official in the British (1898) and in a number of other Pharmacopœias, the dose in the former being 3 to 10 grains in a cachet for internal antisepsis, especially in typhoid and in cholera as a preventative. Its solubility in water is increased by boric acid. Schneider observes that naphthols dissolved in alkaline carbonates have greater disinfectant power than alkaline naphtholates; the former solutions contain naphthol in the free state. He states that staphylococci and typhoid are killed in a short time by 0·5 to 1·0 p.c. of β-naphthol alkaline carbonate solution (Zeitsch. Hyg. 1906, 52, 534).

Ointments containing 10 to 15 p.c. are efficient in scabies and psoriasis. 'Betol,' β-naphthol salicylate, is less soluble than naphthol, and is now seldom used. 'Alphol' is its analogue from α-naphthol, and is very similar.

A number of easily soluble compounds have been introduced, such as the β-naphthol sulphonates, 'Asaprol' or 'Abrastol' (calcium), and 'Alumnol' (aluminium). Helbing states that an aqueous solution of the latter, 1 in 250, prevents all growth of gonococci, pus cocci, and allied bacteria. Bechold (Zeitsch. angew. Chem. 1909, xxii. 2033) finds the odourless and non-poisonous halogen-substituted naphthols more powerful than any disinfectant except HgCl₂, and that tribromonaphthol kills staphylococci in dilutions of 1 in 250,000.

Dihydroxynaphthalene. The 2·3- substituted compound has a relatively high germicidal activity, with a C.A. coefficient of 4·4. The 2·7- derivative has a coefficient of 2·8.

Amidobenzene derivatives. The introduction of $-NH_2$ groups into the ring produces substitutes of low germicidal activity.

Aniline is open to the same objection as the nitro- derivatives; it has a carbolic acid coefficient of 0·57, whilst *o*-toluidine, the next homologue, has a coefficient of 1·00, and *m*-toluidine one of 1·30.

The dyestuffs. A number of aniline dyes are germicidal, owing to their power of penetrating and combining with living tissue. This action is very variable, but it is stated that 1 p.c. prevents development of organisms, whilst 1 in 500 to 4000 retards their growth.

The investigation of the parasiticidal powers of the dyestuffs was conducted by Ehrlich and his pupils in their search for compounds containing strongly developed parasitotropic groupings, but only with feeble organotropic groupings. It was found that tetrazo colours derived from naphthalene-3·6-disulphonic acid, basic dyes of the triphenylmethane series, and certain azocolours were equally effective. Symmetrical colours were found to be less organotropic than unsymmetrical ones.

Methyl violet or 'pyoktanin,' gentian violet, certain auramines, safranine, methylene and toluidine blue have been used in surgery and in malaria. Malachite green, injected into the blood, kills *trypanosoma* in 48 hours (Birt. Med. J. 1904, ii. 1449, 1645; Deutsche Med. Woch. Leipzig, 1906, 21, 463). Methylene blue, with atropine and benzoic acid, according to Lclean (Lancet, May 3, 1902), was the only drug he found of use against *Bilharzia.*

Derivatives of acridine, especially acriflavine-3·6-diamino-10-methyl acridinium sulphate and proflavine-3·6-diamino acridine sulphate, have been shown to be somewhat superior to malachite green when used for wound dressing. Originally prepared for Ehrlich, their selective action on bacteria was first tested at the Middlesex Hospital, London. For wound dressing, the derivatives are made up as soaps, gelatine, or starch mucilages.

Linked benzene derivatives. Both the chemical constitutions and the germicidal activities of the higher boiling tar acid fractions are as yet unknown. The direct linkage of two phenoloid groupings or linkage through $=CH_2$, $=CHOH$, $=CHOX$ where X is an aliphatic group, in some cases elevates the germicidal powers. Linkages through $=CO$ or $=SO_2$ groupings is said to depress the coefficient.

Aromatic nitro- and *halogen substituted compounds,* such as nitro-benzene, have often been

proposed as disinfectants, but are precluded by their odours, poisonous action, and sparing solubility. Trinitrophenol, ' picric acid,' is rapidly fatal in saturated solution (about 1 p.c.) to bacteria and spores, but causes yellow stains, is irritant and very poisonous. Cotton wool, soaked in the solution, is used very successfully in the aseptic treatment of burns ; hence it is recommended by H.M. Inspector of Explosives to keep handy for this purpose. The R.W. coefficient is about 6. Potassium dinitro-ortho-cresol, ' Antinonnin,' 1 in 400, is destructive to all common injurious parasites, and does not injure plants.

Trichlorphenol has been used at Petrograd as a disinfectant. It is said to be 25 times stronger than carbolic acid.

Hydrocarbons.—Petroleum, mainly consisting of hydrocarbons of the paraffin series, has long been a well-known insecticide, and is mentioned by Marco Polo in the 13th century as used to kill acari in mange.

For protecting burns and wounds from exposure, various substitutes for ' ambrine,' consisting essentially of paraffin wax or asphalt with a fatty oil have been suggested (B.M.J. 1917, 789).

A. J. Hull introduces into these burn dressings ' scarlet red,' ' brilliant green,' ' flavine,' and dichloramine-T on account of their antiseptic action.

Naphthalene is feebly antiseptic, but is not a disinfectant It is useful by its odour to drive away domestic insects.

It has been stated that articles are disinfected by dry-cleaning with petroleum benzine, or by benzene. Farrel and Howles (J. Soc. Dyers, 1908, 24, 109, 166), however, find that acting on infected threads for 6½ hours, neither benzene (C_6H_6) nor petroleum-benzine killed *typhosus*, whereas carbon tetrachloride killed it in 30 minutes, whilst ' benzine soap,' dissolved in benzine, has no germicidal power.

Ether is used for sterilising catgut.

Essential oils and **camphors**. Perfumes, chiefly composed of terpenes and their oxidised products (*e.g.* the camphors, menthol, thymol, and eucalyptol), have a limited sanitary value. All of them are very sparingly soluble in water, but impart to it a more or less antiseptic effect Early estimates of their power have not been concordant, chiefly owing to their having been tried variously in aqueous or alcoholic solution, or in suspension. A saturated solution of *thymol* in water (0·3 p.c.) arrests fermentation and putrefaction. Peppermint (containing *menthol* and menthane) has had a high reputation, and a number of recipes for ' plague water,' have it as a basis. The use of hops in brewing partly rests on the power of the essential oil to check fermentation. ' Terebene,' made by the action of H_2SO_4 on terpentine, was once reputed as a disinfectant, but now hardly figures except as terebene soap. Among other artificial products from turpentine are *terpin hydrate* (said by Colpi to arrest the growth of tubercle bacilli in 0·25 p.c. strength), and *terpineol* (anthrax's is stated to be killed by 1 p.c., and staphylococci by 10 p.c. in 60 minutes : (H. Marx, *v. infra* ; *also* D. R. P. 207576, 1908)).

Camphor is much spoken of as a personal prophylactic, but there cannot be sufficient of

the vapour to sterilise the air. It is an ingredient in many remedies for cholera and diarrhœa, and in several ' block disinfectants ' such as ' Sanoscent,' ' Camphortar, &c. *Eucalyptus globulus* and other species which have long been famous as antimalarial, are largely planted on the Continent in marshy districts. The essential oil is decidedly germicidal, having a carbolic acid coefficient of 1·2, and has been given with some success in typhoid, and also against tape- and threadworm.

Pinol is a liquid of similar character from *Pinus pumilo*. H. Marx has investigated the action of various perfumes on anthrax and *S. pyog. aureus* (Centr. Bakt. 1903, [1] 33, 74). Kobert (Chem. Zentr. 1907, 1. 419) finds that the terpenes have, by themselves, in general only a weak antiseptic action. The proportions needed for sterilising exceed the solubility in water, and can only be reached by a spirituous solution or an emulsion.

But it has been recognised, since Schönbein pointed out the fact about 1840, that essential oils have a disinfectant power conferred on them by their slow oxidation in the presence of air and moisture, whereby ozone is produced ; that as long as air and oil are present, the ozone is continually regenerated and absorbed, forming oxidising and antiseptic products, which dissolve in the water, along with peroxide of hydrogen. This was the principle of the ' Sanitas ' patent 274, 1876.

Pyridine, quinoline. and **related bodies.** *Pyridine* is volatile, mixes freely with water, and is strongly insecticide, but has a very unpleasant odour, which has militated against its use in horticulture. Tobacco smoke, indeed, owes its powers, not to nicotine, which is almost entirely decomposed by the heat, but to the products pyridine and its homologues, which are formed. Tessmar destroyed the bacilli of cholera and pneumonia by tobacco smoke passed for 10 to 30 minutes through a tube containing infected nutrient gelatin. Wynter Blyth killed the bacillus of nasal catarrh by 1 p.c solution of pyridine and its homologues (from bone oil), or by tobacco smoke. There is proof that smokers and workers in tobacco enjoy comparative immunity from epidemics, but pyridine inhalations (*e.g.* in asthma and whooping cough) require care, as it is a cardiac depressant. The above experiments confirm the general view that disinfectant preparations containing the basic constituents of coal tar are to be preferred to those which only include the phenols.

Tobacco juice, of course, contains nicotine, and in France is sold as an insecticide under an official guarantee as to its nicotine strength. In England, a solution of the pure base in water is sometimes used as more definite. Richard's cakes for fumigation are nicotine and camphor : the writer found a sample in 1909 to contain 1·17 p.c. of nicotine and to be completely volatile at a gentle heat.

Chinosol is potassium - oxyquinoline - sul - phonate $C_9H_6NO\cdot OSO_3K$, a yellow powder easily soluble in water to an acid yellow solution, which does not stain, has only a slight aromatic odour, is permanent on keeping, is not poisonous, and does not coagulate albumen. It has been patented as a disinfectant, and more especially as an antiseptic. Klein compared its

action on *S. pyog. aureus*, *B. coli* and *anthracis* with that of carbolic acid, and reports that a solution of the latter of 1 in 20 strength is required to kill *aureus* or *coli* in 5 minutes with certainty, whereas chinosol does this in a strength of 1 in 150. Anthrax spores are not appreciably affected in 48 hours by 5 to 6 p.c. carbolic, whereas chinosol of 1 p.c. acts germicidally on them in 5 minutes. In the writer's laboratory, *B. coli* was not sensibly affected after 4 hours by 1 in 1000 chinosol, whilst 1 in 2000 of HgCl₂ produced sterility under the same conditions in 15 minutes, so that it is difficult to explain the much higher powers that some observers have found for chinosol. Thresh and Sowden state that chinosol spray of not less than 1 p.c., is a reliable disinfectant (J San. Inst. Jan. 1903). Houston did not succeed in killing *B. coli* in excréta by 1 in 75, and on linen by 1 in 62 (Practitioner, 1902, 331). On account of its acidity, it acts on iron and steel. Alkaline solutions interfere with its power: the writer showed that a soap containing 5 p.c. of chinosol was inferior to a 0 5 mercuric iodide soap F. G. Muller reports encouraging results with chinosol in leprosy (Zeitsch. Oest Apoth Ver xxxv. 858). 'Cresochin' (Pharm Centralhalle, xxxvii. 247) is said to be a neutral sulphonate of quinoline and tricresol, which is recommended for disinfecting instruments, as it does not darken the steel.

Ichthyol.—Various derivatives from sulphurated tars and fossilised fish or petroleums have been suggested for mild disinfection and the treatment of skin diseases. Ichthyol ammonium ichthyol sulphurated has been compounded with various substances, such as albumen, formaldehyde, and metals, such as silver and mercury, under a variety of names.

Quinine, which has a quinoline nucleus, probably owes its action against fevers as much to its antiseptic power as to its effect on the nervous system.

A. Raal (Pharm. Zeit. 1900, xlv. 569) asserts that strongly fluorescent bodies much increase the action of sunlight on organisms, whilst they are almost inert in the dark. A 1 in 20,000 solution of acridine killed infusoria exposed to sunshine in 6 minutes; in the dark they survived for 24 hours. Similar results were noted with quinine sulphate and with eosin. The inference is that the effect is caused by the fluorescent rays. Fluorescein has been patented as an antiseptic by Turpin, chiefly for toilet preparations (Fr. Pat 346363, 1904). The bromofluoresceins, particularly eosin, are found to have greater power. He claims a large number of other phthalein compounds as disinfectants.

Certain faults of many antiseptics and disinfectants in the free state have led to an immense number of attempts to improve them by converting them into various derivatives. Although the effort to produce new proprietary substances, has given rise to a multitude of often misleading titles, many of these preparations have been proved to have utility. The modifications may be generally classified as follows :—

1. *Metallic salts.*—Compounds with the alkalis or earths are generally less active than the free substance. Other metals have been introduced, with the object of adding their special properties,

as Al for astringency, Zn, Cu, Ag, and Hg for developing germicidal effect; but it must be remembered that a combination of this kind, though it may have some lateral advantages, is commonly weaker than either agent singly. The same remark applies to the two next groups.

2. *Substituted compounds.*—Those with iodine are exceedingly numerous, including a large number which have been improvements on iodoform when it was unduly valued. Where organic radicals (basic like methyl or ethyl, acid like acetyl or benzoyl) are introduced, the physiological properties are usually entirely altered.

3. *Esters*, sulphonic, and other colligated compounds which, while less poisonous or irritant than the parent bodies, slowly yield the latter by gradual decomposition. Several of these have proved of great value.

As already indicated, the proprietary articles of this nature bearing fancy names are very numerous. Since the Privy Council Orders of 1900 and 1902, the uncontrolled sale of liquids containing upwards of 3 p c. carbolic acid or its homologues is prohibited, and the germicidal value of the more insoluble and higher boiling-point tar acids has been recognised. The generality of commercial disinfectant fluids are now practically free from carbolic acid, and, in comparison with the latter, are non-poisonous These disinfectant preparations should not be employed to destroy resistant spores without prolonged exposure; according to the nature and amounts of active ingredients present, they are usually germicidal with non-sporulating organisms in dilutions far greater than is the case with absolute phenol However, the strength of these proprietary articles varies considerably, and beyond the requirements of germicidal value specified in contracts with various authorities, there is at present, unfortunately, no legal control over the efficiency of disinfectants as sold to the public. There are instances of so-called disinfectants which enjoyed great popularity and even were advocated by the medical profession, yet possessed little or no germ-killing power under the conditions in which they would be employed.

Since the adoption of the R.W. test, there has been a steady rise in the efficiency of commercial disinfectants

The Mechanism of Disinfection.—Krönig and Paul, in 1897, first drew attention to the relationship between germicidal action and the ionic concentration of certain germicidal ions such as mercurion, argention, hydrion, and formulated the rule that the germicidal activity of a solution was proportional to the ionic concentration of the germicidal ions. More recent work, such as that of Kitasato, Horrocks, and Winslow, on the common acids, and more especially the development of the organometallic group of disinfectants, indicated that this generalisation was by no means correct. Ehrlich and his pupils attributed to disinfectants the possession of at least two specific properties, the presence of an organotropic and a parasitotropic grouping indicating the 'affinity' of the germicide to living tissue and the parasite or bacterium respectively.

Neither of these theories will serve to

explain the phenomena observed in disinfecting with ionised and unionised solutions, with emulsions and other colloids. Bacterial suspensions must be regarded as suspensoids coated by, or containing, an emulsoid, and are to be classed as definite colloidal systems.

The reactions between agglutin and the bacteria, similar to the reactions between toxins and antitoxins, resemble in many respects either the combination of a very weak acid and a weak base, a view advanced and supported by Arrhenius (' Immunochemie '), or the usual absorption phenomena observed at colloidal surfaces. Although experimental evidence (notably that of Marsden, Nyman, and Chick, carried out at the Lister Institute) is not sufficiently accurate to distinguish between the two, yet the other general characteristics of bacterial suspensions lead us to infer that absorption is the first stage of disinfection. We can thus distinguish between the following types of action :—

(1) Absorption of cations (ionic disinfectants) with simultaneous anion absorption, which may affect the activity.

(2) Absorption of substances in solution, e.g. phenol.

(3) Mutual action between bacteria and other colloids, such as emulsions (tar acids) or suspensoids (colloidal metals). The next stage, common to all, is penetration and chemical attack by the absorbed disinfectant. It is evident that the germicidal activity of a substance after absorption is determined by its penetrative or intradiffusive powers as well as its chemical reactivity or 'parasitotropic' properties. The enhanced germicidal powers of the chloramine is doubtless due to their possession of a reactive $-NH_2$ group, but it is by no means clear that dyestuffs are germicidal on account of their possessing certain parasito-groupings or that their activity is not due to a medium diffusivity accompanied by gradual decomposition into germicidal constituents. It appears probable that more light will be shed on this somewhat complex subject by a close study of the phenomena of absorption and the mechanism of intradiffusion of substances in colloidal material rather than by the development of the concept of ionic activity or postulation of certain parasitotropic groupings or valencies endowed with exceptional and unexpected properties.

Testing of Disinfectants.—Before 1881, when Koch introduced the use of pure cultures, tests depending upon the prevention of putrefactive changes in various organic infusions were mainly employed, and to a great extent the antiseptic or preservative value was noted rather than the actual germ-killing power (*see* first edition of this dictionary). Since then, an increasingly large number of investigators have worked upon practical methods of testing. With the phenolic disinfectants, valuations were made upon the total amount of tar acids present, but the widely differing activity of these bodies, which is also modified according to their physical condition on dilution (in *solution*, tricresol has only one-third the germicidal value of that in *emulsion*), has led to the general adoption of bacteriological tests.

In the *thread* method (Koch), silk threads

are impregnated with the test organism, and exposed for a definite time to the action of the diluted agent, and then, after the removal of adhering disinfectant, sub-cultures are inoculated from the threads to determine the survival or death of the organism (*v.* Lancet, July 30, 1900 ; and J. R. San. Inst. 1907, xxviii.). In place of threads, small garnets can be employed (Krönig and Paul), stones of uniform size being coated from cultures of the organism, and added directly to the disinfectant, sterility being determined by inoculating sub-cultures at intervals (Zeitsch. angew. Chem. 1901, xiv. xv.). The chief points to be considered are (1) time ; (2) age of culture ; (3) choice of medium, reaction of same ; (4) temperature of incubation and (5) of disinfection ; (6) variation in vital resistance of same species and (7) of different species ; (8) proportion of culture to disinfectant. In order to facilitate the comparison of disinfectants, Rideal and Walker (J. R. San. Inst. 1903, 424) suggested their carbolic acid coefficient method as the basis for a standard process. In this test, which has been extensively adopted in England and abroad, the efficiency of the disinfectant is expressed in multiples of absolute phenol performing the same work. It is briefly as follows : add 5 drops of a 24 hours' blood-heat culture of the organism in broth to 5 c.c. of a particular dilution of the disinfectant in sterile distilled water ; shake and take sub-cultures with a platinum loop every $2\frac{1}{2}$ minutes up to 15 minutes ; incubate sub-cultures at $37°$ for 48 hours. Allowing 30 seconds for each operation, four different dilutions of the disinfectant with one carbolic control are tested against the same culture and under strictly comparable conditions. For example :

	Minutes $2\frac{1}{2}$	5	$7\frac{1}{2}$	10	$12\frac{1}{2}$	15
Disinfectant 1 : 500	+	–	...	--	–	–
,, 1 : 550	+	+	–	—	–	–
,, 1 : 600	+	+	+	--	--	–
,, 1 : 700	+	+	+	+	+	–
Carbolic acid 1 : 110	+	+	—	—	—	—

Carbolic acid coefficient $\frac{550}{110}=5$

This test has for many years been officially used by the War Office, Admiralty, India Office and other Government departments at home and in the Colonies. It is impossible in any one test to include the greatly varying conditions of practical disinfection, but numerous modifications of the R.W. coefficient test have been suggested, mainly with the object of testing in the presence of considerable quantities of organic matter. Sterilised sea-water, urine, sewage, starch, and gelatine emulsions, nutrient broth and milk, have been incorporated with the diluting water—also testing with organisms in their natural environment, as with *coli* in sewage, in place of pure cultures. A sedimentation test for emulsified fluids allows a 1 p.c. solution to stand 24 hours before preparing final dilutions for testing (Lancet, Sept. 19, 1908). The ' Lister test ' (C. J. Martin) is made in the presence of 3 p.c. of fæces, previously sterilised; dried, and powdered. Sims Woodhead and Ponder (J. Path. and Bact. 1909, 148) replace the inoculating loop by platinum spoons, used with a special sterilising apparatus, and extend the

time to 30 minutes. A mean coefficient is taken for two values obtained at the beginning and end of the experiment with *B. coli* and sub-culturing into McConkey's bile-salt fluid. The Lancet (Nov. 1909) has suggested, in conjunction with the above method, a chemical analysis for the valuation of emulsified fluids as follows : 10 grams of disinfectant with 100 c.c. of water and 15 grams baryta, are heated for 30 minutes at 100° under a reflux condenser, then cooled and decanted through asbestos, washing with warm baryta water ; the tar acids are extracted with ether from an aliquot portion of the filtrate, after adding calcium chloride and acidifying with HCl, dried at 38°, weighed, and their bromine absorption determined. Neutral hydrocarbon oils are extracted from the baryta residue with acetone, and the insoluble soaps and resins treated with HCl and shaken out with ether. For estimation of water, 25 grams of the sample are acidified with 10 c c. of 10 p.c. H_2SO_4 and shaken with 25 c c of white petro-leum spirit, taking the volume less 10 c c. of the aqueous layer after standing. In presence of the higher phenoloids, the weight of tar acids obtained is too low. The coefficients obtained for *B. coli* were found to be approximately one-third of the difference between the percentage of tar acids and the bromine value.

In the United States, the National Hygienic Laboratory method of L. Anderson and T. B. McClintic (1912) is now widely adopted. The method, which follows closely the R.W. in technique, differs in the following points of detail : The standard temperature of medication of 20°C., instead of 18°C., is adopted. 0·1 c c. of broth culture is added to 5 c c. of disinfectant solution instead of 5 drops. The coefficient is determined from the mean of the following two reactions :—

Weakest strength of disinfectant which kills in 2½ minutes

Weakest strength of phenol that kills in the same time

and the similar ratio for death in 15 minutes.

From time to time various modifications have been introduced in which solid media such as nutrient agar have been substituted for broth. An emulsion of an agar slope culture of an organism is made with the various disin-fectant dilutions and phenol controls, whilst the sub-culturing is either performed direct into agar slopes or spread out on agar plates, thus permitting counts to be made. Nutrient agar made up with fresh meat is certainly less inhibiting than standard broth, whilst certain advantages attend the use of plates, giving approximate data as to the number of organisms surviving after specified periods of disinfection, as against the 'end point' method of the fluid media tests. These advantages are nearly entirely negatived by the difficulty of obtaining a uniform agar streak growth emulsion for medication, and the extra labour involved in plating a number of tests.

The germicidal power expressed in terms of carbolic acid with *B. typhosus* is shown for a number of disinfectant substances in the follow-ing table ; while most of the figures are Rideal-Walker carbolic acid coefficients, some of the results have been obtained by modifications of

the original test as noted, and these are obviously not comparable with the others.

Agent	Germicidal value	Observer
Absolute alcohol	less than 0·1	F. 1905
Acetic acid	0·6	R. 1907
Acetyl-coumaric acid	4·5	
Aniline	0·57	
o-Toluidine	1·00	
m-Toluidine	1·3	
Benzoic acid	about 5·0	R. 1910
Boric acid	less than 0·1	W. 1904
Bromine water	64	R. 1910
Cadmium chloride	1·55	R. 1911
Cadmium sulphate	1 0	R. 1911
Chinosol	0·15–0·30	Various observers
Chlorine water	28	R. 1910
Copper sulphate (calculated on $CuSO_4$)	2·0	R. 1910
Cresylic acid commercial	3·7	R. 1908
o-Cresol	2·1	
p-Cresol	2·4	M. & C. 1912
m-Cresol	2·0	
Eucalyptol	1·2	L. 1904
Formaldehyde	0·55	R. 1907
Ditto	0·75	W. 1904
Formic acid	5·7	R. 1907
Guaiacol	0·9	L. 1904
Trimethylene-thoxy-phenol	4·0	W.
Quinol	1·1	M. & C.
Catechol	0 48	M. & C.
Hydrochloric acid	1 58	F. M. 1906 (with fæces and urine)
Hypochlorites (calculated on 'available chlorine')	146–220	Various observers
Ditto with 50 p.c. urine	8	K. 1906
Iodine water	100	R. 1910
Iodine trichlor-ide	94	R. 1909
Lactic acid	1·8	R. 1910
Mercuric chloride	400–3540	Various observers
2.3-Dihydroxy-naphthalene	4·4	
2.7-Dihydroxy-naphthalene	2·8	
Potassium per-manganate	42	do.
Picric acid	6·0	
Pyrogallic acid	0·22	M. W. B. 1906
Resorcin	0·30	do.
Silver nitrate	15·8	R. 1910
Sodium bisul-phate	4·1	R. 1908
Sulphate	0·09	
Zinc chloride	0·15	W. 1906

M. W. B., Meredith Wynter Blyth ; F. M., Firth and Mac-fadyen ; F., Major Fowler ; K., Klein ; L., Lodwidge ; M. & C., Morgan and Cooper ; R., Rideal ; W., Walker.

The extremely high values once given for mercuric chloride were due to the powerful inhibitory action of the traces carried over with the sub-cultures in the inoculations.

S. & E. R.

DISPARGEN. Trade name for a form of colloid mercury.

DISPERMIN. Trade name for piperazine.

DISSOCIATION v. CHEMICAL AFFINITY.

DISTHENE v. KYANITE.

DISTILLATION. The object of distillation is the separation of a volatile liquid from a non-volatile substance, such as pure water from sea-water, or more commonly the separation of two or more liquids of different volatility.

The apparatus required consists essentially of four parts : a still or boiler, A (Fig. 1), in which
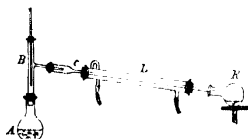
FIG. 1.

the liquid is boiled ; an upright tube or head, B ; a condensing tube, C, sloping downwards and cooled by suitable means—a Liebig's condenser, L, through which a current of water is passed, being generally employed in the laboratory ;
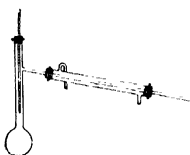
FIG. 2.

lastly, a receiver, R, to collect the distilled liquid The form of apparatus shown in Fig 2 is convenient for many purposes ; the still, the head, and the condensing tube are sealed together in one piece The still is usually heated by the flame of a Bunsen burner ; for very volatile and inflammable liquids a water-bath is generally used, but the rate of distillation can be better regulated by a very small flame in contact with the bottom of the still ; the Liebig's condenser is unnecessary for liquids which boil above 160° or 170° if the condensing tube is fairly long. For many purposes, notably for distillation under reduced pressure, it is convenient to employ an electrically heated coil of platinum, German silver, or nichrome wire as the source of heat (Richards and Matthews, J. Amer. Chem. Soc. 30, 1282 ; 31, 1200; Beckmann, Zeitsch. physikal. Chem. 64, 506 ; Bailey, J. Amer. Chem Soc 33, 447 ; Rosanoff and Easley, ibid. 31, 964)

If the temperature at which the liquid boils is to be ascertained with accuracy—and this is generally the case in fractional distillation, especially in the final purification of a liquid –the following points should be attended to :—

1. The thermometer should be carefully calibrated, and it would be a great advantage if all thermometers were compared with an air thermometer, for different kinds of glass expand very differently when heated, and therefore two thermometers, constructed of different varieties of glass, will give different readings, especially at high temperatures.

2. The zero point of the thermometer should be redetermined from time to time. It is a good plan to heat the thermometer for several hours to about 300° or 360° before calibrating it ; the subsequent changes of zero point, which other-

wise might be considerable at high temperatures, are thereby greatly reduced (Crafts, Compt. rend. 95, 910 ; also several earlier papers). Thermometers treated in this manner may now be purchased.

3. All thermometers, except those which do not register temperatures higher than 60° or 70°, should contain nitrogen to prevent volatilisation of mercury in the heated stem ; if the thermometer is provided with a small bulb at the top, rise of pressure owing to compression of the gas in the thermometer is avoided.

4. The thermometer should, if possible, be so placed in the apparatus that not only the bulb but also the column of mercury in the stem is surrounded by the vapour of the boiling liquid ; otherwise the following correction, which, at the best, is somewhat uncertain, must be applied :—

N = length of column of mercury in scale degree not heated by vapour.

T = temperature of vapour (the approximate temperature directly read on the thermometer is usually sufficiently accurate).

t = mean temperature of column of mercury not heated by vapour. This temperature may be approximately ascertained by attaching a small thermometer to the other by means of thin indiarubber bands or wire, with its bulb at about the middle of the unheated column

Correction : add 0 000143(T−t)N.

The coefficient 0 00016 is usually employed, but Holtzmann pointed out that this is too high, and adopted the number 0 000135 Thorpe, however (Chem. Soc. Trans. 37, 159), has shown that the coefficient 0 000143 gives the best results.[1] The table for the correction of thermometer readings is taken from Thorpe's paper, and shown in next column.

For further information v. article on THER-MOMETERS.

5. When the amount of liquid in the bulb is very small, the vapour is liable to be superheated by the flame, and unless the bulb of the thermometer is thoroughly moistened with condensed liquid, too high a temperature will be registered. If a very little cotton wool or, for temperatures above 230°, a little fibrous asbestos be wrapped round the bulb of the thermometer, it remains thoroughly moist, and with a pure liquid the thermometer registers a perfectly constant temperature until the last trace of liquid in the bulb has disappeared (Ramsay and Young, Chem. Soc. Trans. 47, 42).

6. The barometer should always be read, and corrected to 0°, and in a long distillation or in unsettled weather it should be read frequently, for the boiling-point varies greatly with the pressure. The observed boiling-point is corrected to that under normal pressure by means of the formula $\theta = c(760-p)(273+t)$, where θ is the correction in centigrade degrees to be added to the observed boiling-point, $t°$; c is a constant ; and p is the barometric pressure. For the

[1] Rimbach (Ber. 22, 3072) has constructed tables of corrections by interpolation from experimental data up to 220° for two kinds of thermometer graduated in degrees, and up to 100° for thermometers graduated in tenths of a degree. All these thermometers were constructed of Jena glass, and from the results it would appear that the form of the thermometer, and doubtless also the nature of the glass, have a notable influence on the magnitude of the correction.

majority of liquids the value of c may be taken, without serious error, to be 0·00012 ; but for water and the alcohols it is about 0·00010, and for a few liquefied gases it is considerably higher. A table of corrections was first given by Crafts (Ber. 20, 709). The values of c for a large number of substances have been collected and

T-t	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
10	0·29	0·27	0·26	0·24	0·22	0·21	0·20	0·19	0·17	0·16	0·14	0·13	0·11	0·10	0·09	0·07	0·06	0·04	0·03	0·01
20	0·57	0·54	0·51	0·49	0·46	0·43	0·40	0·37	0·34	0·31	0·29	0·26	0·22	0·20	0·17	0·14	0·11	0·09	0·06	0·02
30	0·86	0·82	0·77	0·73	0·68	0·64	0·60	0·56	0·51	0·47	0·43	0·39	0·34	0·30	0·26	0·21	0·17	0·13	0·09	0·04
40	1·14	1·09	1·03	0·97	0·91	0·86	0·80	0·74	0·69	0·63	0·57	0·52	0·47	0·40	0·34	0·28	0·23	0·17	0·11	0·05
50	1·43	1·36	1·29	1·22	1·14	1·07	1·00	0·93	0·86	0·79	0·71	0·64	0·60	0·50	0·43	0·36	0·29	0·21	0·14	0·07
60	1·72	1·63	1·54	1·46	1·37	1·29	1·20	1·12	1·03	0·94	0·86	0·77	0·70	0·60	0·51	0·43	0·35	0·25	0·17	0·08
70	2·00	1·90	1·80	1·70	1·60	1·50	1·40	1·30	1·20	1·10	1·00	0·90	0·80	0·70	0·60	0·50	0·40	0·30	0·20	0·10
80	2·29	2·17	2·05	1·94	1·83	1·72	1·60	1·49	1·37	1·26	1·14	1·03	0·91	0·80	0·68	0·57	0·45	0·34	0·23	0·11
90	2·54	2·45	2·31	2·17	2·05	1·93	1·80	1·66	1·54	1·42	1·30	1·16	1·03	0·90	0·77	0·64	0·51	0·39	0·26	0·13
100	2·86	2·72	2·57	2·43	2·29	2·15	2·00	1·84	1·71	1·58	1·43	1·29	1·14	1·00	0·85	0·71	0·57	0·43	0·28	0·14
110	3·15	2·99	2·83	2·67	2·51	2·36	2·20	2·04	1·89	1·73	1·58	1·42	1·26	1·10	0·94	0·79	0·63	0·47	0·31	0·16
120	3·43	3·26	3·09	2·92	2·74	2·57	2·40	2·23	2·06	1·89	1·71	1·54	1·37	1·20	1·03	0·86	0·69	0·51	0·34	0·17

tabulated by Young (Chem. Soc. Trans. 81, 777 ; Fractional Distillation, 15).

The various parts of the simple apparatus (Figs. 1 and 2) may require modification under certain circumstances.

The still.—For larger quantities of liquid, a tin or copper vessel is preferable to glass.

The head.—The modifications of this part

of the apparatus will be considered under *Fractional distillation.*

The condenser.—For very volatile liquids, the condensing tube must be cooled by ice or a freezing mixture (pounded ice and salt or ice and concentrated hydrochloric acid, &c.). In this case, a spiral or ' worm ' tube should be used (Fig. 3). Condensation of moisture in the receiver is prevented by the drying tube a. V CONDENSERS.
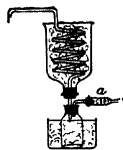
FIG. 3.

The receiver.—If a liquid boils at a very high temperature, or if it suffers decomposition at the ordinary boiling-point, it may be necessary to distil it under reduced pressure. For cases of simple distillation, the apparatus shown in Fig. 4 may be employed, but if the
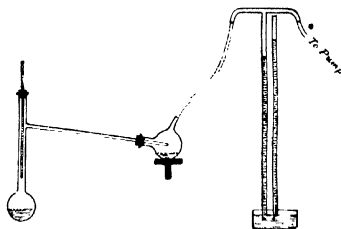
FIG. 4.

distillate is to be collected in separate portions, as in fractional distillation, the removal of the receiver would necessitate the admission of air into the apparatus and a fresh exhaustion after each change. This inconvenience may be obviated by the employment of stopcocks arranged in such a manner that air may be admitted into the receiver and a fresh one put in its place while the distillation bulb remains exhausted (Thörner, Ber. 9, 1868 ; F. D. Brown, Chem. Soc. Trans. 35, 554 ; L. T. Thorne, Ber. 16, 1327 (Fig. 5) ;

FIG. 5.

Lothar Meyer, *ibid.* 20, 1834 ; Wade and Merriman, Chem. Soc. Trans. 99, 984 ; Rosanoff and Easley, *l.c.* ; Rosanoff, Bacon and White, J. Amer. Chem. Soc. 36, 1806). Or, again, a series of receivers on a revolving stand placed under an exhausted bell-jar may be employed (Gorboff

and Kessler, Ber. 18, 1363; Brühl, *ibid.* 21, 3339 (Fig. 6)).

Many liquids absorb moisture from the air or are acted upon by oxygen, and in these cases special precautions must be taken, the moist air in the apparatus being expelled and replaced by dry air, carbon dioxide, nitrogen, or hydrogen;
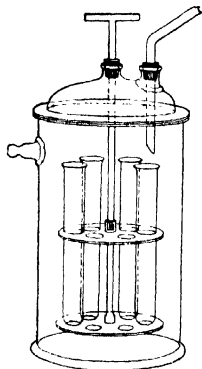
FIG. 6.

the receivers must also be protected by drying tubes. (For example, *v.* Thorpe, Chem. Soc. Trans. 47, 120; Young, *ibid.* 59, 923.)

Theory of distillation.—Investigations of the vapour pressures of liquids have thrown much light on the subject of distillation. If a pure liquid be confined in the space above the mercury in a barometer tube, it will evaporate until the pressure of its vapour—measured directly by the depression of the mercury column—has reached a definite amount, which, for a given substance, and, if liquid be still present, depends solely on the temperature. From the readings of pressure at various temperatures we may construct a curve to illustrate the relations of temperature to pressure for a given substance, but this curve has a twofold meaning, for it represents not only the vapour pressures at definite temperatures, but also the boiling-points of the liquid under definite pressures. Thus the vapour pressure of pure water at 100° is 760 mm. of mercury at 0°; and under a pressure of 760 mm. water boils at 100°. Again, the vapour pressure of water at 0° is 4·6 mm., and if the pressure in a distillation bulb containing water be reduced to 4·6 mm., the water will boil at 0°. The truth of this general statement was conclusively proved by Regnault (Mém. de l'Academie, 21 and 26).

Regnault also investigated the behaviour of a few mixed and heterogeneous liquids, which he divided into three classes : (1) liquids which are quite or almost insoluble in each other ; (2) liquids which are miscible only within certain limits ; (3) liquids which mix in all proportions. Regnault employed both the statical and dynamical methods of investigation ; that is to say, he determined, on the one hand, the vapour pressures of the liquids at various temperatures

in the barometer tube, and, on the other hand, the boiling-points of the liquids under various pressures.

The behaviour of two liquids, A and B, when brought into contact with each other, must be affected (*a*) by the attraction of the like molecules ; those of A for each other, and those of B for each other ; and (*b*) by the mutual attraction of the molecules of A and B. If the attraction of the unlike molecules is relatively very slight, it may be expected that the liquids will be non-miscible, or nearly so, as in the case of benzene and water. If the attraction of the unlike molecules is greater, but still relatively small, miscibility within limits may be expected, as, for example, with aniline and water. In such cases there is frequently slight expansion and slight absorption of heat on admixture. Comparing together various pairs of liquids, as the mutual attraction of the unlike molecules increases relatively to that of the like molecules, the following changes may be expected ; (*a*) increasing and finally infinite miscibility ; (*b*) slight expansion, diminishing to zero, and followed by increasing contraction ; (*c*) diminishing absorption of heat, changing to increasing heat evolution These changes do not, in many cases, run strictly *pari passu*, and among liquids which are miscible in all proportions, it is not unusual to find a small amount of contraction attended by a slight absorption of heat, as, for example, when a little water is added to normal propyl alcohol, but when certain compounds, such as chlorobenzene and bromobenzene, which are chemically closely related, are mixed together, there is no appreciable change of volume or temperature. For such substances it is probable that the different molecular attractions, A for A, B for B, and A for B, are very nearly equal, and that the relation suggested by Galitzine (Wied. Ann. 41, 770 ; and by D. Berthelot, Compt. rend. 126, 1703), namely, that $a_{A\ B} = \sqrt{a_A . a_B}$, holds good, where $a_{A.B}$ represents the attraction of the unlike molecules, and a_A and a_B the respective attractions of the like molecules.

It would appear, then, that there are two very simple cases : I. that in which the liquids are non-miscible ; II. that of two infinitely miscible and closely related liquids which show no heat or volume change on admixture.

I. It was found by Regnault that when two non-miscible liquids are placed together over the mercury in a barometer tube, the observed vapour pressure is equal to the sum of the vapour pressures of the two liquids when heated separately to the same temperature. It is only necessary that both substances should be present in sufficient quantity, and that the tube should be shaken or sufficient time allowed for the evaporation of the heavier liquid. The liquids evaporate independently of each other, and Dalton's law of partial pressures is therefore applicable to the distillation of non-miscible liquids. Each vapour behaves to the other as an indifferent gas, and the boiling-point of each liquid depends on the partial pressure of its own vapour. The temperature is necessarily the same for both liquids, and the total pressure, if the distillation is carried out in the ordinary

manner, is equal to that of the atmosphere. The boiling-point is, therefore, that temperature at which the sum of the vapour pressures of the components is equal to the atmospheric pressure. For example, at 90·23° the vapour pressure of water is 530·1 mm. ; and that of chlorobenzene is 210·1 mm. ; total, 740·2 mm. ; and it was found that when chlorobenzene and water were distilled together under a barometric pressure of 740·2 mm., the temperature varied only between 90·25° and 90·35°, until there was scarcely any chlorobenzene left in the residue, when it rose rapidly to 100°. The boiling-point of a pair of non-miscible liquids is necessarily lower than that of the more volatile component, and may be far lower than that of the less volatile.

The process of distillation with steam is very frequently employed in the case of substances of high boiling-point, which are insoluble or only slightly soluble in water, such as aniline or nitrobenzene. (For the application of steam distillation to the preparation of ethereal oils, v. von Rechenberg, Theorie der Gewinnung und Trennung der ätherischen Oele durch Destillation, Schimmel & Co 1910)

The composition of the vapour—and therefore of the distillate—from two non-miscible liquids, like the vapour pressure and boiling-point, is independent of the relative amounts of the components, provided that both are present in sufficient quantity and that evaporation can take place freely. Calling the vapour densities D_A and D_B, and the vapour pressures at $t°$ p_A and p_B, there will be, in a litre of the mixed vapour, 1 litre of A at $t°$ and p_A mm., and 1 litre of B at $t°$ and p_B mm. The weights of vapour will therefore be :

$$\frac{0·0899 \times D_A \times 273 \times p_A}{(273+t) \times 760} \text{ and } \frac{0·0899 \times D_B \times 273 \times p_B}{(273+t) \times 760}$$

respectively, and the relative weights will be $\frac{D_A \times p_A}{D_B \times p_B}$ (Naumann, Ber. 10, 1421, 1819, 2014, 2099 ; Brown, Chem. Soc. Trans. 35, 547).

The vapour density of chlorobenzene is 56·2, and that of water is 9 ; and at 90 23° the relative weights of vapour will be

$$\frac{m'_A}{m'_B} = \frac{56·2 \times 210·1}{9 \times 530·1} = 2·475,$$

and the percentage weight of chlorobenzene will be 71·2. In the actual experiment to which reference has been made, the percentage of chlorobenzene in the distillate was found to be 71·4. Both boiling-point and vapour composition agree well with the calculated values.

II. The vapour pressure of a mixture of two infinitely miscible liquids which are chemically closely related to each other, or, probably, for which $a_{A.B} = \sqrt{a_A.a_B}$, is given by the formula $100p = Mp_A + (100 - M)p_B$ where M is the molecular percentage of A, and p, p_A, and p_B are the vapour pressures of the mixture and of A and B respectively, at the same temperature, $t°$. In other words, the relation between vapour pressure and molecular composition is represented by a straight line (Van der Waals,

Proc. Roy. Acad. Amsterdam, 3, 170 ; Young, Chem. Soc. Trans. 81, 768 ; Young and Fortey, ibid. 83, 45 ; Zawidski, Zeitsch. physikal. Chem. 35, 129 ; Vanstone, Chem. Soc. Trans. 97, 429 ; Price, ibid. 115, 1116). The relation has been found to hold accurately for chlorobenzene and bromobenzene, and with very slight error for other pairs of closely related liquids.

In order to calculate the boiling-points of all mixtures of two such liquids under a given pressure, p, the vapour pressures of each must be known at all temperatures between their respective boiling-points under that pressure. The percentage molecular composition of mixtures which would exert the vapour pressure p must then be calculated at a series of temperatures between these limits by means of the formula $M = 100 \dfrac{p_B - p}{p_B - p_A}$. Lastly, the values of M must be plotted against the temperatures, when the curve drawn through the points will give the required relation between boiling-point and molecular composition. In the cases examined, the agreement between the observed and calculated results is quite satisfactory.

The relation between the composition of a liquid mixture and that of its vapour (distillate) has been the subject of many experimental investigations (Brown, Chem. Soc. Trans. 35, 547 ; 39, 304 ; Lehfeldt, Phil. Mag. (v.) 46, 42 ; Zawidski, Zeitsch. physikal. Chem. 35, 129 ; Carveth, J. Phys. Chem. 3, 193 ; Winkelmann, Wied. Ann. 39, 1 ; Linebarger, J. Amer. Chem. Soc. 17, 615 ; Gahl, Zeitsch. physikal. Chem. 33, 179 ; Rosanoff, Lamb, and Breithut, ibid. 66, 349 ; Rosanoff and Easley, J. Amer. Chem. Soc. 31, 953 ; Rosanoff, Bacon and White, ibid. 36, 1803 ; Rosanoff, Bacon and Schulze, ibid. 36, 1993 ; Rosanoff and Bacon, ibid. 37, 301 and 1072). Special attention may be directed to the last four of these papers. Unfortunately, however, it is only in a very few cases that the mixtures investigated consisted of closely related liquids (Young, Sci. Proc. Roy. Dubl. Soc. 15, N.S., 667). In the discussion of their results, Lehfeldt and Zawidski made use of formulæ which they derived from a general equation proposed independently by Duhem and by Margules, and it is to be noted that both formulæ, in the simplest cases, can be reduced to one originally given by Brown, $\dfrac{m'_A}{m'_B} = c.\dfrac{m_A}{m_B}$, where m'_A and m'_B are the relative weights of the two substances in the vapour, m_A and m_B the relative weights in the liquid, and c is a constant. From Zawidski's formula it would follow that $c = \dfrac{p_A}{p_B}$. So far as experimental evidence is available, it would appear that Brown's formula is applicable to mixtures of liquids for which $a_{A.B} = \sqrt{a_A.a_B}$, and that for closely related liquids $c = \dfrac{p_A}{p_B}$.

Another formula, which gives good results, is proposed by Rosanoff, Bacon and Schulze (loc. cit.).

When the components of a liquid mixture are not chemically closely related, the relation between vapour pressure and molecular composition is not, as a rule, represented by a straight

line, but by a curve, and, in all probability, the form of the curve depends on the relation between $a_{A,B}$ and $\sqrt{a_A.a_B}$, as shown in Fig. 7. That is to say, when

$$a_{A\,B} < \sqrt{a_A.a_B},\ 100p > Mp_A + (100-M)p_B,$$

and *vice versa*.

The greater the difference between $a_{A\,B}$ and $\sqrt{a_A.a_B}$ the greater will be the curvature; and it will be seen that, for any given values of p_A and p_B, if the deviation from straightness exceeds a certain limit, there must be a point of maximum or minimum pressure on the curve. It is obvious, also, that the smaller the difference between p_A and p_B, the smaller will be the deviation required to give a maximum or minimum pressure. If $a_{A\,B}$ is so much smaller than $\sqrt{a_A.a_B}$ that the two liquids are only partially miscible, the maximum pressure will not be represented by a single point, but by a horizontal line forming part of the curve

The influence of chemical relationship is well seen by the behaviour of the monhydric aliphatic alcohols towards water. These alcohols may be regarded as derivatives of water, formed
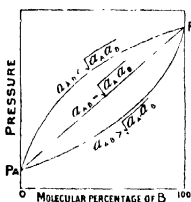
by the replacement of a hydrogen atom by the group C_nH_{2n+1}; the smaller the alkyl group, the closer is the relationship of the alcohol to water. At the ordinary temperature methyl alcohol is miscible with water in all proportions, as also are ethyl and propyl alcohols; normal butyl and *iso*butyl alcohol are only partially miscible with water; and the solubility of the higher alcohols in water diminishes with rise of molecular weight, cetyl alcohol, for example, being practically insoluble. The volume and heat changes on admixture with water similarly indicate that the attraction of the unlike molecules diminishes as the molecular weight of the alcohol increases. Lastly, the deviation of the vapour pressure curves from straightness increases (Konowalow, Wied. Ann. 14, 34), as may be seen from Fig. 8.

(The temperatures are such that the vapour pressure of each pure alcohol is 400 mm.)

The boiling-points of liquids which are not closely related cannot, as a rule, be calculated by means of the formula $M = 100\dfrac{p_B - p}{p_B - p_A}$. If, as is usually the case, the vapour pressures of the mixtures are higher than are given by the formula $100p = Mp_A + (100 - M)p_B$, the observed boiling-points will be lower than the calculated; if the vapour pressures are lower, the boiling-points will be higher. Moreover, when there is a point of maximum pressure on the curve which shows the relation between vapour pressure and molecular composition, there must be a point of minimum temperature

on the boiling-point—molecular composition curve, the composition of the mixture which exerts a maximum vapour pressure, p, at $t°$ being the same as that of the mixture which has the minimum boiling-point, $t°$, under the pressure p. So, also, two substances capable of forming a mixture of minimum vapour pressure can also form a mixture of maximum boiling-point.

Such mixtures of either minimum or maximum boiling-point, when distilled, boil at a constant temperature without change of composition, like pure substances, and they have frequently been mistaken for chemical compounds. The composition, however, depends on the pressure, which would not be the case with a definite compound; and, moreover, mixtures of minimum boiling-point are formed owing to the relatively
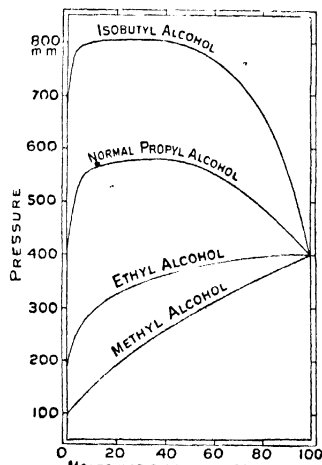
Fig 8.

small attraction of the unlike molecules for each other. A very striking example of the influence of pressure on the composition of the mixture of constant boiling-point has been observed by Wade (Chem. Soc. Trans. 99, 997), in the case of ethyl alcohol and water. Under normal pressure the mixture of minimum boiling-point contains 4·43 p.c. of water. At higher pressures the percentage of water is slightly higher; at lower pressures it is smaller, and it is remarkable that the diminution in the percentage of water becomes more and more rapid as the pressure falls, so that below 80 mm, no mixture of minimum boiling-point is formed at all. V. also Merriman, *ibid.* 103, 628 and 1790.

In the case of three liquids, if each of the three possible pairs is able to form a mixture of minimum boiling-point, it may happen that a particular mixture of all three liquids will boil constantly at a lower temperature than will any of the pairs or single liquids. Thus benzene and

· water form such ternary mixtures of minimum boiling-point with ethyl, n-propyl, isopropyl, and tertiary butyl alcohols (Young, Chem. Soc. Trans. 81, 707; Fortey and Young, ibid. 81, 739).

A table of mixtures of constant boiling-point is given in Young's Fractional Distillation, 67–69. Other mixtures have since been discovered by Wade (Chem. Soc. Trans. 85, 938; 87, 1656; v. also 95, 1842), and by other observers. The subject has been exhaustively studied by Lecat, La Tension de Vapeur des Mélanges de Liquides; l'Azéotropisme (Brussels, 1918). Lecat has collected the data published by other chemists, and has himself investigated more than 2000 mixtures, and has discovered and tabulated a very great number of binary mixtures of minimum boiling point, and a moderate number of binary mixtures of maximum boiling-point, and of ternary mixtures of minimum boiling-point. He has also observed the dependence of the composition of the azeotropic mixtures on the pressure in a considerable number of cases.

The composition of the vapour from a mixture of liquids which are not closely related, cannot, as a rule, be calculated from the vapour pressures of the components and the composition of the liquid, but for purposes of interpolation the formulae of Lehfeldt, Zawidski or Rosanoff may be found useful ($l c_e$) Rosanoff, Bacon and Schulze ($l c$) have discovered a simple and very useful solution between the partial pressures (number of molecules) of the components in the vapour and the vapour pressures of the mixture and of the two pure substances. They give a formula which is applicable even when mixtures of maximum or minimum vapour pressure are formed

Fractional distillation. It has been stated that Brown's formula, $\dfrac{m'_A}{m'_B} = c\dfrac{m_A}{m_B}$, is applicable to mixtures of all closely related liquids so far investigated, and that, in all probability $c = \dfrac{p_A}{p_B}$. The value of c is necessarily such that the vapour is richer than the liquid in the more volatile component. The first portion of distillate obtained by condensation of the vapour will, therefore, be richer, and the

residual liquid will be slightly poorer in that component. Continuing the distillation, the vapour evolved from the residual liquid will again be richer than the liquid in contact with it in the more volatile component, though poorer than the first portion of vapour. If successive portions of vapour be condensed, the percentage of the more volatile component in the distillates or fractions will steadily diminish, until, if the constant c differs greatly from unity, the residue will consist of the less volatile liquid in a pure or very nearly pure state. As the distillation proceeds, the temperature will, therefore, rise until, if c has a high value, the boiling-point of the less volatile component is reached.

If the fractions obtained in the first distillation were redistilled, each of them could be separated into smaller fractions, the first richer and the last poorer in the more volatile component, and by a process of systematic fractional distillation it should, theoretically, be possible to effect a separation of both components.

A mathematical and experimental investigation (Barrell, Thomas, and Young, Phil. Mag. (v.) 37, 8) of the behaviour on distillation of mixed liquids which follow Brown's law, showed that with two components it is the liquid of higher boiling-point which is the easier to separate; and that if there are three or more components boiling at fairly equal intervals the substances of intermediate boiling-point are the most difficult to separate, and the least volatile substance is the easiest. See also Lord Rayleigh, Phil. Mag [5] 4, 527, and Rosanoff, Baker and Schulze, J. Amer. Chem. Soc 36, 1993

The method employed for the fractional distillation of a mixture of two liquids can best be explained by taking a concrete example. A mixture of 100 grams of benzene (b p. 80·2°) and 100 grams of toluene (b p. 110·6°) was slowly distilled, and the distillate was collected in a convenient number of fractions, the receivers being changed when the boiling-point reached certain definite previously arranged temperatures, the actual readings being corrected for barometric pressure and for errors in the thermometer scale The results of the first four fractionations, and also of the ninth, are given in Table I.

TABLE I.

Number of receiver	Final temperature (corrected)= t	Weight of fraction = ΔW				t	ΔW
		I.	II.	III.	IV.	IX.	
Pure benzene	° —	—	—	—	—	80·2	10·20
1	81·2	—	—	12·95	31·55	80 3	45·00
2	83·2	—	3·80	24·80	23·90	80·6	17·55
3	86·2	—	33·85	22·75	16·20	81·4	7·20
4	89·2	9·75	22·30	13·50	9·55	83·5	4·50
5	92·2	51·80	19·65	11·80	8·00	88·0	3·30
6	95·4	28·85	13·60	9·15	5·80	95·4	2·75
7	98·6	21·20	12·95	7·30	5·35	102·8	2·60
8	101·6	12·80	9·05	6·75•	4·65	107·3	2·85
9	104·6	11·45	8·90	6·30	3·85	109·4	3·15
10	107·6	14·15	10·80	7·95	5·85	110·2	3·45
11	109·6	13·45	9·80	8·95	7·40	110·5	7·00
12	110·6	24·90	30·75	33·05	30·50	110·6	5·75
Pure toluene	(110·6)	10·90	22·95	31·35	42·10	(110·6)	72·10

• In the first distillation the temperature rose almost at once to 86° (corr.), and the first portion of distillate was therefore collected in receiver 4. On the other hand, the temperature reached 110·6° before the whole of the liquid had come over; the residue, therefore, consisted of pure toluene.

The distillate in receiver 4 was now placed in a smaller flask and distilled, fractions being collected in receivers 2, 3, and 4. When the temperature reached 89·2°, the flame was removed, and the contents of receiver 5 were added to the residue in the still. The distillation was recommenced, and fractions were collected in receivers 3, 4, and 5, the flame being removed when the temperature reached 92·2°. The distillation was continued in a similar manner until, after addition of the contents of receiver 12, the temperature rose to 110·6°, when the residue of pure toluene was added to that from the first fractionation. The third and fourth fractionations were carried out like the second. In the subsequent fractionations the temperature ranges of the middle fractions were gradually increased and those of the lowest and highest fractions diminished. It was not until the ninth fractionation that pure benzene began to be collected. Eventually 81·4 grams of pure benzene and 88·8 grams of pure toluene were recovered.

Full details of the systematic fractional distillation of mixtures of two liquids and three liquids, and of more complex mixtures, are given in 'Fractional Distillation,' 114–143.

If the components of a mixture are not closely related, the composition of the vapour cannot, as a rule, be calculated by Brown's formula, but even in such cases the percentage of the more volatile component in the vapour will be greater than in the liquid, and the separation by fractional distillation is theoretically possible, unless the deviation of the vapour pressure-composition curve from straight-
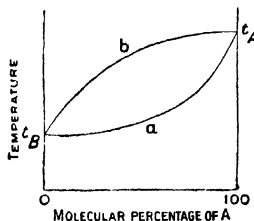
FIG. 9.

ness is so great that a mixture of maximum or minimum vapour pressure is formed.

For mixtures to which Brown's law is applicable, it may be stated quite generally that the greater the difference between the boiling-points of the compounds, 'the more readily can a separation be effected by fractional distillation, but for other mixtures the form of the curve representing the relation between boiling-point and molecular composition, if known, must be taken into account. If the curve for two components were of the form a

(Fig. 9), the substance of higher boiling-point could be separated very easily, but the more volatile component only with great difficulty, if at all. On the other hand, if the curve were of the form b, nearly horizontal at the higher temperature, the more volatile component would be comparatively easy, and the less volatile difficult to separate. The first case is frequently met with, the second seldom. With curves of the form c and d (Fig. 10) it would not, under any conditions, be possible to separate
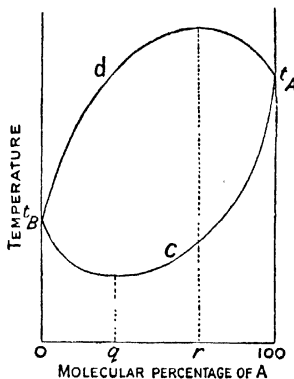
FIG. 10

both components by distillation of any given mixture, but it would be possible to separate the mixture of minimum or maximum boiling-point from that component which was in excess. In a case represented by curve c, where the minimum temperature corresponds to the molecular composition q, the distillation might proceed in either of three ways : (1) If the liquid mixture had the composition q, it would distil unchanged in composition at the constant minimum temperature ; (2) if the molecular percentage of A were less than q, the liquid would tend to separate into two components, the more volatile of which would be the mixture of minimum boiling-point, and the less volatile the substance B ; (3) if the molecular percentage of A were greater than q, the components separable by distillation would be, first, the mixture of minimum boiling-point, and, second, the liquid A. A well-known case of this kind is that of normal propyl alcohol and water ; the boiling-points under normal pressure are : water, 100° ; n-propyl alcohol, 97·2° ; mixture of minimum b.p. 87·7°.' This mixture contains 43·2 molecules p.c. of the alcohol ; it was described for many years as a hydrate of propyl alcohol. If the curve had the form d, the mixture would distil like a pure liquid if it had the composition r, or it would tend to separate into two components, the first being either A or B, according as the molecular percentage of A in the original mixture was greater or less than r, and the second the mixture of maximum boiling-point. Formic acid and water behave in this manner, as shown by Roscoe (Chem. Soc.

Trans. 13, 146; 15, 270). Boiling-points : water 100°; formic acid, 99·9°; mixture of maximum b.p., 107·1°; molecular percentage of acid in mixture, 56·7°.

If, as with ethyl alcohol and water (Fig. 11), the mixture of constant boiling-point distils at nearly the same temperature as one of the two pure liquids, it is impossible to separate that liquid in a pure state by distillation. In this
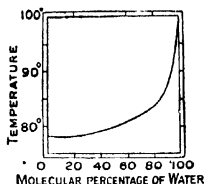
Fig. 11.

case, as the curve is exceedingly flat at the lower temperature (Noyes and Warfel, J. Amer. Chem Soc. 23, 463), it is practically impossible to separate the mixture of minimum boiling-point (containing 4·43 p.c. by weight of water) in a pure state even when water is in excess, although it is quite easy to separate pure water from dilute spirit.

The correct interpretation of the results of the fractional distillation of a complex mixture may be rendered very difficult by the following causes : (1) the presence of two components boiling at nearly the same temperature ; (2) the presence of one or more components in relatively very small quantity ; (3) the formation of mixtures of constant boiling-point. It is only by plotting the total weights of distillate against the temperatures, or by dividing the weight of each fraction, Δw, by its temperature range and tabulating the ratios $\Delta w/\Delta t$, that the results are likely to be understood, and in any case, the existence of a mixture of constant boiling-point may not be discovered, and it may be difficult to decide whether a distillate collected at a practically constant temperature consists of a single pure substance or of two liquids boiling at nearly the same temperature.

All the above difficulties are met with in the fractional distillation of petroleum, which contains homologous and isomeric paraffins, polymethylenes and their alkyl derivatives (naphthenes) and aromatic hydrocarbons, Russian petroleum being relatively rich, and American petroleum poor in naphthenes and aromatic hydrocarbons. When American petroleum was carefully distilled, it appeared at first as though the distillate coming over between the ordinary temperature and 40° contained only a single component, boiling at about 33°; but by systematic fractional distillation with a very

efficient still-head, it became evident (Fig. 12) that two components, isopentane, b.p. 27·95°, and normal pentane, b.p. 36·2°, were present (Young, Chem. Soc. Trans. 71, 440). Again, in the early fractionations there appeared to be no indication of the presence of any component boiling between 40° and 60°, but by tabulating the values of $\Delta w/\Delta t$, it was seen that a very small quantity of a liquid boiling at about 50° was present, and a distillate coming over almost constantly at 49·5° was eventually obtained. A chemical and physical investigation of this distillate showed, however, that it was a mixture of pentamethylene and a hexane of low boiling-point. The presence of benzene in American petroleum is indicated by the formation of dinitrobenzene, when the distillate from, say, 60° to 80° is treated with nitric and sulphuric acids (Schorlemmer, Annalen, 127, 311). But when the petroleum was carefully fractionated, it was found that the small fraction coming over at about 80° yielded no dinitrobenzene, the greater part being obtained from the fractions below 70°. This anomaly is explained by the fact that benzene forms a mixture of constant boiling-point with n-hexane, coming over at almost the same temperature as the paraffin. The amount of benzene being relatively small, the whole of it distils over at the low temperature. In Russian petroleum the percentage of benzene is so much greater that some of it comes over at its true boiling-point, 80·2° (Young, Chem. Soc. Trans. 73, 905).

(For a detailed discussion of the interpretation
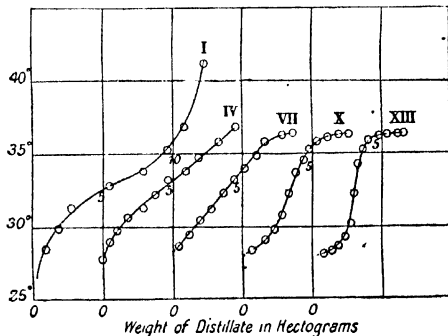
Fig. 12.

of the results of the fractionation of complex mixtures, v. Fractional Distillation, chap. 19.)

Improved still-heads. It would be quite impossible to effect really difficult separations by means of the ordinary apparatus employed for distillation, and various modifications of the still-head have been devised in order to increase its efficiency. Even when the separation is an easy one, much time and material may be saved by the employment of efficient still-heads. Great progress was made in the improvement of the still-head in commerce—notably for the better separation of alcohol from weak spirit—before

any advance was made in the laboratory. It will, however, be more convenient to consider first those forms of apparatus which are suitable for laboratory purposes.

In choosing or constructing a still-head, the first point to be considered is its efficiency in separating the components of a mixture. It frequently happens, however, that the quantity of liquid available is small, and it is therefore important that the quantity of condensed liquid in the still-head at any moment shall be as small as possible. If the residual liquid is to value, it is also of importance that the condensed liquid in the still-head shall all return to the still after the source of heat is removed.

In comparing the efficiency and usefulness of different still-heads, it is necessary always to distil a mixture of the same composition; and the rate of distillation must always be the same, because the efficiency of any still-head is greatly diminished by increasing the rate. In the comparisons mentioned in this article, equal weights of pure benzene and pure toluene were employed, and the distillate was collected at the rate of one drop per second. Unless otherwise stated, 50 grams of the mixture were distilled.

Of all possible forms, the plain vertical still-head is the least efficient. During distillation, as the vapour rises up the cylindrical tube, the outer part of it comes in contact with the condensed liquid flowing down the sides of the tube. Since the tube is constantly losing heat by radiation and by conduction to the surrounding air, this liquid is constantly cooled and fresh condensation constantly goes on, the outermost layer of vapour probably condensing almost completely with little change of composition. The central portion of vapour rises rapidly up the tube, and can only reach the liquid by diffusion or by convection currents, and much of it may pass through the still-head without reaching the liquid at all; the condensed liquid, on the other hand, flows rapidly back to the still. In order, however, that a satisfactory separation of the components may take place, as much of the vapour as possible should come in contact with the hot condensed liquid, so that equilibrium, as regards composition, may be brought about all through the tube.

The efficiency of a plain vertical still-head is, roughly, proportional to its length. For tubes of equal length the efficiency is lowest when the internal diameter is about 14 mm. On the other hand, the quantity of liquid and vapour in the still-head increases regularly with the width of the tube; it is therefore better to use very narrow rather than very wide tubing.
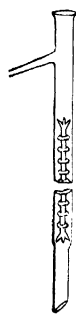
Better contact between liquid and vapour, and therefore greater efficiency, is ensured by sloping the middle part of the tube, the extremities being kept vertical, and the efficiency is further improved by bending the sloping portion so as to form a spiral. In Young's 'rod and disc' still-head (Fig. 13), the downflow

FIG 13

of part of the condensed liquid is greatly retarded by the discs on the central glass rod, and this liquid is protected from the cooling

action of the air; at the same time, eddies and cross-currents are produced in the vapour. The increase in efficiency caused by the introduction of the easily constructed rod with discs is very marked. Wurtz (Ann. Chim. Phys. iii. 42, 129) recommended a vertical tube with a series of bulbs blown on it, and Young has shown that the efficiency is somewhat increased and the amount of liquid in the still-head is greatly diminished by blowing pear-shaped instead of spherical bulbs on the tube (Fig. 14). The 'rod and disc' and 'pear' still-heads are specially suitable for liquids of high boiling-point.

Greater efficiency, combined with diminished condensation of liquid in the still-head, is attained in Young's 'evaporator' column, one section of which is shown in Fig. 15. The
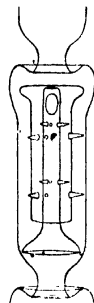
FIG. 14.   FIG. 15.

vapour rises up the inner tube, passes down between the inner and middle tubes, and up again between the middle and outer tubes, and so reaches the section above. The liquid condensed in the upper part of the still-head falls in drops from the depression at the top of the section on to the flattened top of the inverted middle tube, and spreads itself over its surface, falling again in drops from the bottom of this tube. The temperature of the vapour passing through the inner tube of any section being higher than the boiling-point of the condensed liquid falling on to the inverted tube, re-evaporation takes place to some extent, and, if there is much difference between the boiling-points of the components of the mixture being distilled, ebullition may actually occur. The quantity of condensed liquid in the still-head is thereby greatly reduced. The 'evaporator' still-head is specially suitable for accurate work where great efficiency is required (Chem. Soc. Trans. 75, 679; Wade and Merriman, ibid. 99, 984).

The 'Hempel' still-head (Zeitsch. anal. Chem. 20, 502) consists simply of a wide vertical tube, filled with glass beads of special construction, and constricted below to prevent the beads from falling out. A short, narrower vertical tube with side delivery tube is fitted by means of a cork into the wider tube. The advantages of the Hempel apparatus are simplicity and efficiency, but the amount of liquid in the still-head is excessive. Raschig employs thin rings

of copper or some other metal in place of the glass beads, the depth of a ring being about equal to its diameter. Lessing uses split rings, the metal being also bent inwards across the ring, thus (↑). These rings are easier to construct and give a larger surface; they give very good results. Rings are much lighter than beads.

The results obtained with various still-heads are given in Table II.

TABLE II.

Nature of still-head or dephlegmator	Plain vertical, 5·1 mm. diameter	Plain vertical 14·0 mm. diameter	Plain vertical 25·7 mm. diameter	'Rod and disc' 14 mm. diameter	'Pear'	'Evaporator'	'Evaporator'	'Evaporator'	'Hempel' with 200 beads	Glinsky	Le Bel-Henninger	Young and Thomas	Young and Thomas
Number of discs, bulbs, or sections	—	—	—	20	13	3	5	8	—	3	3	3	18
Vertical height in cm.	62	62	62	62	62	46	62	78	58	30	43	51 [1]	130
Final temperature of fraction						Percentage weight of distillate.							
83·2	—	0·1	—	1·4	3·0	12·80	26·00	35·85	20 6	1·1	0·5	0·6	38·8
86·2	0 5	0·1	0·2	18 1	26·2	21·15	12·35	6·50	15·4	11·7	17·8	21·8	4·1
89·2	22·2	12·8	20·0	15 8	11 0	7 50	5·60	2·90	7·2	17·3	15·9	14·3	1·9
92·3	16·5	21 5	18·8	9·7	5·8	4·80	3·25	2·15	3·4	11·9	8·8	7·8	1·8
95·4	9·2	11 0	9 2	6·1	5·2	3 35	4·95	1·40	3·2	7·5	7·2	5·0	1·3
98·5	7·2	8 9	7·2	4·2	2·4	2·70	1·30	1 15	2 2	5·6	4·3	4·7	1·2
101·6	5 8	7·4	4·7	3·8	2·4	2·30	1·80	1 05	1 8	5·7	4·8	4·0	0·9
104·6	5·5	6·2	5·9	4·2	2 8	2·50	1·50	1·15	2·9	5·6	4·6	3·6	1·2
107 6	5·9	7 3	6·4	4·3	3·6	3 50	2·45	1·60	3·2	8·9	5 5	5·2	2·0
110·0	7 1	8·4	10·0	8 0	5·0	6 50	4 20	3·95	6 8	13·7	9·8	7·3	4·0
110 6	8·9	9·0	7·2	6·6	11·0	10 50	11·40	9·60	8·4	2 5	6·8	9·8	8·1
Pure toluene by difference	11·2	7·4	10·4	17·8	21 6	22·40	27 90	32 70	24·9	8·5	14·0	15·9	34·7
Weight of liquid and vapour in still-head	1 05	1·55	3·15	2 35	2·6	2·70	4 55	6·25	7·85	2·8	5·85	2·8	12·1

In many of the still-heads employed on the large scale, for example in the Coffey still (Fig. 28), the condensed liquid is caused, by means of suitable obstructions, to collect into shallow pools, and the ascending vapour has to force its way through these pools; very good contact is thus brought about between vapour and liquid at definite intervals. The excess of liquid is carried back from pool to pool, and finally to the still by suitable trapped reflux tubes. It is convenient to reserve the term 'dephlegmator' for this class of still-head. The 'Le Bel-Henninger' (Fig. 16) and the 'Glinsky' (Fig. 17) dephlegmators have been very frequently employed for laboratory work, but they do not give good results when small quantities of liquid are distilled; the dephlegmators of Brown (Chem. Soc. Trans. 37, 49) (Fig. 18) and of Young and Thomas (ibid. 75, 679) follow the principle of the Coffey still more closely, and are much better in this respect.

In a comparison of the Glinsky, Le Bel-Henninger, and Young and Thomas dephlegmators, each with three sections, it was found that when 400 grams of the mixture of benzene and toluene were distilled, there was not a great difference in efficiency, but the Glinsky was the least satisfactory. With 50 grams of the mixture the differences (Table II.) were
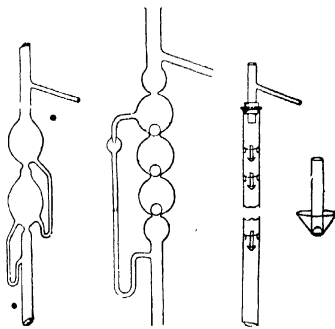
FIG. 16.   FIG. 17.   FIG 18.

quite noticeable, and with 25 grams they were greatly accentuated. With the Glinsky

[1] Unnecessarily long.

column the highest temperature reached was only 107·6°, and the residue, when distilled from a very small bulb, came over between 102·2° and 110·4°. No pure toluene was therefore obtained, and the residue left in the still was distinctly less pure than the last portion of distillate collected. With the Le Bel-Henninger column the highest temperature was only 107·25°, and the residue began to boil at 105·7°; with the Young and Thomas column the temperature just reached 110·6°, and the residue began to boil at 110·4°. The 'rod and disc,' the 'pear,' and the 'evaporator' still-heads gave better results when only 25 grams of the mixture were distilled, the residue in each case consisting of pure toluene. These results show that for small quantities of liquid the Young and Thomas dephlegmator gives much better results than the Glinsky or Le Bel-Henninger, but that none of them is so satisfactory as the other still-heads.

In order that a dephlegmator may give the best results, the following requirements should be fulfilled : 1. It should be possible to greatly increase the number of sections without seriously increasing the fragility of the apparatus   2. As the amount of condensed liquid flowing back at any level is greatest at the bottom and least at the top, it follows that, in order to form a pool, more complete obstruction is required at the top of the column than at the bottom.   3. Since the amount of condensed liquid in the still-head should be as small as possible consistently with efficiency, the reflux tubes should not be wider—in that part which is filled with liquid during distillation—than is necessary to carry back the liquid freely, and the traps should be no deeper than is required to prevent the ascending vapour from forcing its way through them.   On the other hand, the upper part of the reflux tubes should be wide, so as to facilitate the entrance of the liquid.   4. There should be a rapid flow of condensed liquid through the reflux tubes, otherwise the change in composition of the liquid in these tubes will lag behind that of the distillate.   5. There should be a reflux tube connecting each section with the one below it, so that the change in composition may be regular from top to bottom of the column.   In this respect the Glinsky dephlegmator is entirely wrong in principle.   6. When the distillation is completed, the residual liquid should return as completely as possible from the still-head to the still.   In this respect the dephlegmators as a class are less satisfactory than the other still-heads.

By surrounding the still-head with water or any other liquid, the temperature of which is kept as little above the boiling-point of the more volatile component as will allow of vapour passing through, a considerable improvement in the separation is effected.   The temperature of the bath, however, requires very careful regulation if the boiling-points of the components are near together, or if one component is present in large excess, for in either case a fall of a fraction of a degree would cause complete condensation of the vapour, while a slight rise of temperature would prevent any condensation from taking place, and there would be no fractionation whatever.   In constructing a regulated temperature still-head, it is advisable to bend the tube into

the form of a spiral, because its effective length may thus be greatly increased without unduly adding to the height of the bath, and also because the spiral form is more efficient than the vertical.   But Rosanoff and Bacon (J. Amer. Chem. Soc. 37, 301) find that an annular form of regulated temperature still-head is far more efficient and quite as simple as the spiral tube form.   This class of still-head was first recommended by Warren (Annalen, Suppl. 4, 51).   A better apparatus was described by Brown (Chem. Soc. Trans. 37, 49 ; 39, 517) (Fig. 19).   A combination of a regulated temperature still-head and dephlegmator was employed by Young and Thomas (ibid. 71, 440) for the separation of normal and iso-pentane from petroleum.
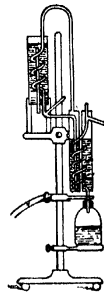
Experiments to test the relative efficiency of these various forms of apparatus have been made by Kreis (Annalen, 224, 259 ; Claudon, Bull. Soc. chim. 42, 613 ; Brown, Chem. Soc. Trans 37, 49 ; Young, ibid. 75, 679 ; Fractional Distillation, chaps. 10, 11, and 14 ; Friedrichs, Zeitschr. Angew. Chem., 32, 341).

Continuous distillation of wort has long been carried out on the large scale by means of the Coffey still (Fig. 28).   In 1902 Carveth (J. Phys. Chem. 6, 253) and Lord Rayleigh (Phil. Mag. vi. 4, 521) independently suggested apparatus intended for use in the laboratory.   The liquid to be distilled (or its vapour) is introduced continuously into the middle part of a long spiral or other still-head, the lower part of which is prevented, by means of a liquid or vapour-bath, from cooling below the boiling-point of the less volatile of the two components, while the temperature of the upper part is prevented, by means of a liquid bath, from rising above the boiling-point of the more volatile component. Lord Rayleigh obtained good results in the distillation of weak spirit.   It is probable that the method might be made applicable to the distillation of mixtures of three components (Fractional Distillation, 189).   See also Rosanoff, U. S. Pat. 1171464.   Constant temperature zones are utilised to obtain products of the desired composition.

As many of the stills used in the arts are described under the headings ALCOHOL, BENZENE, PARAFFIN, &c., it will be unnecessary here to give a minute description of all of them, but an account of the principles underlying the different methods will not be out of place.

The still is usually made of copper or some other metal, but for special purposes other materials must be employed.   Thus for the distillation of sulphuric acid, vessels of glass or platinum are used ; for nitric acid, cast iron is found to be the best material ; stoneware or glass stills are employed for bromine and iodine ; and so on.

The still may be heated by the free flame

FIG. 19.

of a furnace or by steam. Fig. 20 shows an arrangement for heating a still with steam, which may be above the atmospheric pressure.

When only a rough separation of the constituents of a complex mixture is required, as in
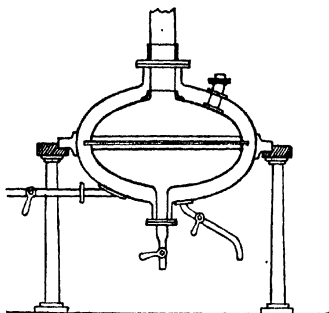
Fig. 20.

the preliminary distillation of coal tar, dephlegmators or rectifiers are not employed, but the vapours pass directly from the still to the condenser.

For the better separation of the components of a mixture, modified still-heads are employed. A simple apparatus, devised by Mansfield for the distillation of tar oils, is shown in Fig. 21 ; the vapours are partially condensed in the still-head A, which is cooled by water, and the condensed liquid flows back into the still B, the purified vapour passing on to the condenser C.
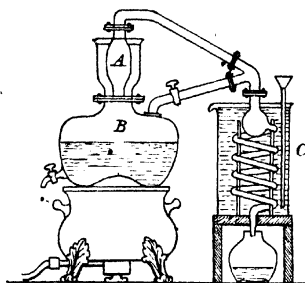
Fig. 21.

A more perfect separation is effected by Coupier's apparatus (Fig. 22). In addition to the column A, there is a series of bulbs, B, B, placed in a cistern containing brine, which may be heated by steam by means of the pipe C. The vapour— of benzene, for example—partially freed from less volatile substances in the column, is further purified by partial condensation in the bulbs, the condensed liquid flowing back by the tubes D, D into the column, while the purified vapour passes on to the condenser by the pipe E.

A very similar arrangement is seen in the French column apparatus (Fig. 23). The liquid is heated by a steam coil in A; the vapour is

partially purified in the rectifier B; it is further freed from the less volatile components in the
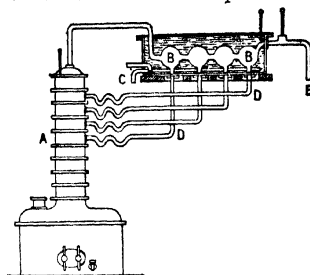
Fig. 22.

condensing apparatus C, and finally reaches the condenser D.
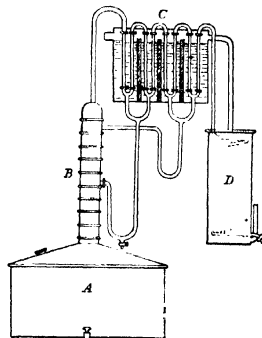
Fig. 23.

In Savalle's apparatus also the vapours pass first through a dephlegmator or analysing column, then through a surface or multitubular condenser, which is provided with a water supply, so regulated that its temperature is about that of the boiling-point of the liquid required ; the liquid condensed in the regulated-temperature still-head returns to the dephlegmator, and the purified vapour passes on to the cold condenser.

In most of the still-heads employed on the large scale, the vapour first passes through a dephlegmator, the construction of which varies considerably in different cases. Dubrunfaut's dephlegmator, employed in the French column apparatus, is shown in Fig. 24. Two others, devised by Savalle, are represented in Figs. 25 and 26.
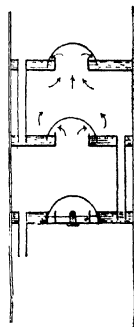
Fig. 24.

In the Ergot dephlegmator an arrangement somewhat similar to the dome (Fig. 24) is used, but a large number of these domes are placed in each tray, and the condensed liquid is made to follow a zigzag course from the circumference to the centre of each tray.
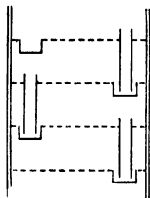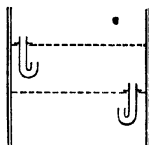
FIG. 25.   FIG. 26

The principle of the still-head in the Pistorius still is quite different. The vapour, entering a section (Fig. 27) of the still-head, is deflected from centre to circumference by the flat dome; it then passes back to the centre above the dome, and is partially condensed by the water in the shallow vessel above. It may be pointed out that if, in the Pistorius still-head, the 'roof'

of the section were depressed at the centre instead of the circumference, the condensed liquid would drop on to the flat dome below, and the arrangement would then be somewhat
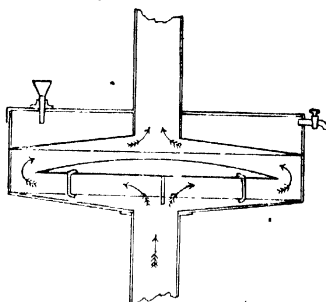
FIG. 27.

similar to that of the 'evaporator' still-head (Fig 15). In all probability the efficiency of the still-head would thereby be greatly increased. Kubierschky (Ger. Pat. 269995. 1913) has devised an excellent column in which the liquid
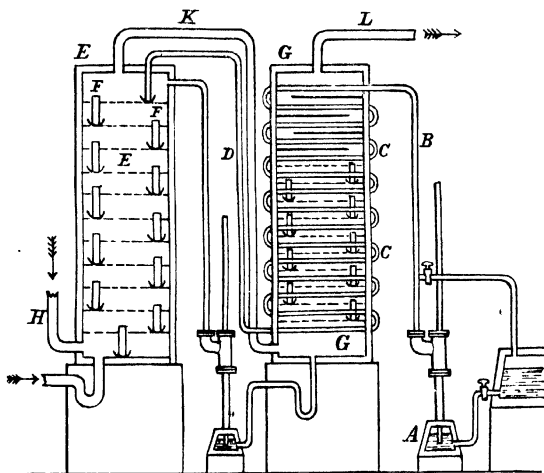
FIG. 28.

falls in drops through perforated plates, whilst the vapour passes freely upwards and downwards, travelling from centre to circumference and from circumference to centre alternately, coming into intimate contact with the falling drops.

A simple and efficient still-head has been described by Foucar (Eng. Pat. 19999 of 1908). The column consists essentially of a helical septum which traverses the annular space

between two concentric cylinders. The vapour from the still passes up the long spiral passage before reaching the condenser. The inner cylinder can, if desired, be used as a thermostat, the column then acting as a regulated-temperature still-head. Dutton (J. Soc. Chem. Ind. 38, 45 T.) has described a still-head, suitable for laboratory work, somewhat similar in principle to Foucar's. A spiral of wire is wound round an inner closed tube which fits quite loosely in the

outer tube of the still-head. But excessive condensation, with consequent priming, must be prevented by covering the tube with a thick layer of cotton wool. The still-head is stated to give very good results.

A. Hirsch (J. Ind. Eng. Chem. 1910, 2, 409) recommends the use of a differential condenser in the still-head, in the form of a spiral of metal tubing, through which a current of water is regulated initial and final temperature is caused to flow. The apparatus works easily and well so long as the temperature of the vapour leaving the still-head is considerably lower than that of the vapour entering it; but the difficulty of regulation increases greatly as this temperature-difference diminishes.

For work on the large scale Hirsch recommends the introduction of a differential condenser between the lower and upper parts of a rectifying column

In England, the Coffey still is largely used; it differs considerably from those described, inasmuch as there is no large boiler, and the heat is supplied, not from an outer fire or steam-jacket, but by the condensation of steam in the wort; moreover, the process is continuous. The essential parts of the apparatus are shown in Fig. 28 (p. 568). The wort is pumped from a reservoir A, up the pipe B, and passes down the zigzag pipe CC, where it is heated by the ascending vapours, then up the pipe D, from which it is discharged into the column E It is prevented from falling through the perforated plates of the column or analyser by the ascending vapours, but falls through the pipes F, F, from one plate to another until it reaches the bottom, when it is allowed to escape. Meanwhile, steam is passed into the analyser E by the pipe H, and causes the wort to boil, so that by the time it has reached the bottom it is completely deprived of alcohol. The ascending vapours force their way through the perforated plates of the analyser, a portion of the aqueous vapour being condensed by each washing, and the descending wort being thereby heated. On reaching the top of the column, the concentrated alcoholic vapour passes down the pipe K into the rectifier, and there ascends through similar perforated plates; but in the rectifier it is not washed by wort, but by the weak alcohol formed by the previous condensation of vapour. This dilute alcohol, on reaching the bottom of the rectifier, flows off into a reservoir, from which it is pumped into the top of the analyser, where it mixes with the descending wort. In the upper part of the rectifier there are simply shelves, which compel the vapour to take the same zigzag course as the pipe which conveys the wort downwards. The purified and concentrated vapour then passes through the pipe L to the condenser. In modern continuous stills of the Coffey type there are special arrangements for the separation of (a) volatile impurities such as aldehyde, (b) pure rectified spirit, (c) fusel oil. For details the articles on ALCOHOL, etc., should be consulted. S. Y.

DISTYRENE C₁₆H₁₆. Produced by heating styrene (q.v.) with hydrochloric acid at 170° (Erlenmeyer, Annalen, 135, 122). Also, together with distyrenic acid and carbon dioxide, by prolonged boiling of cinnamic acid with diluted sulphuric acid (Fittig, Ber. 12, 1739–1744; Erdmann, Annalen, 216, 179–199).

A colourless optically inactive oil, with a blue fluorescence, which gradually disappears; sp.gr. 1·016 at 15°; b.p. 311°. On prolonged boiling yields toluene, isopropylbenzene, and some styrene; whereas metastyrene, produced from styrene on keeping, or heating in sealed tubes at 200° (Kovalevsky, Annalen, 120, 66), or with aqueous sodium bisulphite at 110° (Miller, ibid. 189, 341), passes almost quantitatively into styrene at 320° (Stobbe and Posjnak, ibid. 371, 259–286).

Distyrene yields benzoic acid on oxidation with chromic acid; and a crystalline dibromide C₁₆H₁₆Br₂ (m.p. 102°) on brominating in carbon disulphide solution.

According to Stobbe and Posjnak (Annalen, 371, 287–302), distyrene is αγ-diphenyl-Δᵅ-butene

$$C_6H_5-CH=CH-CH(CH_3)-C_6H_5$$
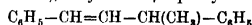
Distyrene disulphonic acid (dicinnamene disulphonic acid) C₁₆H₁₄(SO₃H)₂, described by Lange as obtained on heating γ-truxillic acid with sulphuric acid (Ber. 27, 1410–1415), is therefore not a derivative of distyrene.

Solid distyrene; m.p. 124°; obtained by distilling cinnamic acid or its calcium salt (Engler and Leist, Ber. 6, 256; Miller, Annalen, 189, 340), and by passing C₆H₅·C₂H₃Br₂ over red-hot lime (Radziszewski, Ber. 6, 494), has been shown by Erlenmeyer (Annalen, 372, 249–251) to be stilbene.

DISULPHO ACID S. *Delta acid,* 1-*Naphthyl-amine-*4 : 8-*disulphonic acid v.* NAPHTHALENE.

DITA BARK. *Satween* (Ph. J.' Trans. [3] 7, 110). The bark of *Alstonia scholaris* (R. Br.), an apocynaceous tree found in India, the Philippines, Eastern Australia, and tropical Africa (Ber. 11, 2234).

According to Harnack (ibid. 11, 2004; Chem. Soc. Trans. [2] 36, 332), it contains only one base, *ditaine,* a basic glucoside, having the composition C₂₂H₃₀N₂O₄; but Hesse (Annalen, 203, 144; Ber. 13, 1750; Pharm. J. [3] 11, 251, 331) found in it three bodies: *ditamine,* C₁₆H₁₉NO₂; *echitamine* (ochitammonium hydroxide), C₂₂H₂₈N₂O₄,H₂O, melting with decomposition at 106° (this base is identical with Harnack's *ditaine*); and *echitenine* C₂₀H₂₇NO₄, a brown amorphous mass, melting above 120°, soluble in chloroform, alcohol, and ether. It dissolves in nitric acid with the production of a purple-red colour which quickly passes through green into yellow.

The milky juice of this tree has the same properties as guttapercha; when inspissated it softens in boiling water, is soluble in turpentine and chloroform, and receives and retains impressions. A decoction of the bark is used as an astringent tonic.

DITAÏNE *v.* DITA BARK.

DITHION. Trade name for sodium dithio-salicylate: used as an antirheumatic.

DITTANY. The root of *Dictamnus albus* (Linn.) (ord. *Rutaceæ*), a native of the south of Europe. It contains a volatile oil, and also resin, bitter extractive matter, and gum; and was formerly employed in medicine, especially for the treatment of epilepsy (Aldis, Lond. Med. Gaz. 19, 142).

'*Cretan Ditany*' is the common name for *Origanum dictamnus* (Linn.), a native of the Levant.

DIURETIN. A compound of sodium

theobromine and sodium salicylate (*v.* SYNTHETIC DRUGS).

DIVICINE *v.* VICINE.

DIVI-DIVI. Divi-divi consists of the dried pods of the *Cæsalpinia coriariæ* (Willd.), a tree 20–30 feet high, found in the West Indies and Central America. The pods are about 3 inches long and ¾ inch broad, are very thin, and frequently resemble in shape the letter S. From 40 to 45 p.c. of tannin is present, which consists of ellagitannin and probably also gallotannin. Extracts of this material have a somewhat unfortunate tendency to ferment, with simultaneous development of a deep-red colouring matter; but this can be prevented to some extent by the use of antiseptics. Divi-divi is largely imported for the preparation of leather, and is also employed for black dyeing, but its use is far more limited in this latter respect than myrobalans.   A. G. P.

DOCIMACY or **DOCIMASY.** (*Docimasie*, Fr.) Originally the act or art of examining by test (δοκιμασία, a test), applied in metallurgy to experiments made to determine the nature and purity of a metal; in pharmacy, to the testing of medicines and poisons; in medical jurisprudence, to the different proofs to which the lungs of a new-born child are subjected, for the purpose of ascertaining whether it was born alive or dead (Dunglison). Usually employed in chemistry as synonymous with assaying.

n-**DODECANEDICARBOXYLIC ACID**

$$CO_2H(CH_2)_{12}CO_2H$$
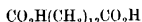
Prepared by hydrolysing the diethyl ester obtained by the electrolysis of an aqueous solution of the monoethyl ester of suberic acid (Brown and Walker, Annalen, 261, 123); or by the oxidation of chaulmoogric acid, obtained from chaulmoogra seeds (Barrowcliffe and Power, Chem. Trans. 1907, 568); m.p. 123°.

DODECATOIC ACIDS $C_{12}H_{24}O_2$.

1. *Lauric acid*, found by Marsson in laurel fat, a glyceride obtained from *Laurus nobilis* (Linn.) (Marsson, Annalen, 41, 330); also present in cocoa-nut oil (Görgey, *ibid.* 66, 295), in pichurin beans, in Dika bread, and in the fruit of *Cylicodaphne sebifera* (Oudemans, Zeitsch. Chem. 1867, 256); m.p. 43·5; (m.p. 47·5°–48°, Levene and West); sp.gr. 0·883/20° and 0·875/43·6°; b.p. 225·5° (100 mm.).

2. *Hordeic acid* is found among the products of the distillation of dried barley with dilute sulphuric acid; forms crystalline plates; m.p. 60° (Beckmann, J. 1855, 513).

DOG-TOOTH SPAR. The scalenohedral form of calcspar (*v.* CALCITE or CALCSPAR).

DOLERITE. An igneous rock composed essentially of plagioclase-felspar (labradorite to anorthite) and augite, and of the same general chemical and mineral composition as the coarse-grained plutonic gabbros and the fine-grained volcanic basalts, but intermediate in texture between these two extreme types. Other minerals may also be present, especially olivine, giving the varieties olivine-dolerite, enstatite-dolerite, hornblende-dolerite, mica-dolerite, and quartz-dolerite. Accessory minerals, usually present, are magnetite and ilmenite; and secondary minerals, produced by alteration, include quartz, calcite, epidote, chlorite, and serpentine. Dolerites occur as intrusive veins,

dykes, and sills; and very often they pass imperceptibly into basalts. The texture may be coarse enough for the individual mineral to be distinguishable to the unaided eye, or it may be so fine that these can only be distinguished in thin sections under the microscope. In the latter case the rock is compact and dark greenish-black or black in colour. Often, owing to the presence of secondary minerals, the colour is distinctly green, and the rock is then frequently included under the general term 'greenstone.' The specific gravity ranges from 2·8 to 3·0, and the crushing strength is about 1500 tons per square foot. The following analyses are of dolerite from I, Rowley Regis, Staffordshire; II, Clee Hill, Shropshire; III, quartz-dolerite from the Whin Sill, Co. Durham (including MnO 0·16, CO_2 0·19, P_2O_5 0·25, FeS_2 0·49); IV, olivine-dolerite from Skye (including MnO 0·17, BaO 0·06, P_2O_5 0·17).

	I.	II.	III.	IV.
SiO_2 . .	49·0	48·4	51·22	50·33
TiO_2 .	2·8	3 1	2·42	1·81
Al_2O_3 .	15·3	13 4	14·06	19·97
Fe_2O_3 .	2 6	4·0	4·32	2·81
FeO .	8 2	8·5	8·73	6·23
CaO .	8·2	8·6	8 33	8·03
MgO .	4 9	6·5	4·42	3·24
K_2O .	.2·6	2·1	1·25	1·19
Na_2O	2·5	3·1	2 55	4·30
H_2O .	3·3	2 2	1·28	1·86

Dolerites are of wide distribution and are much quarried for road-metal and paving-setts. Being difficult to work and of a dull colour, they are not much used as building stones (*v.* DIABASE).
                                        L. J. S.

DOLOMITE. This term includes both dolomite-spar and dolomite-rock, both of which are often referred to simply as dolomite. They bear the same relation to one another as calcite (calc-spar) to limestone, and as quartz to quartzite; these being cases in which a single mineral species builds up a rock-mass. The name dolomite, after the French geologist, D. G. Dolomieu (1750–1801), was first applied to the rock, being later extended to the crystallised mineral. The rock is now often referred to as dolomitic limestone or magnesian limestone.

The pure mineral (*Dolomite-spar*) is a double salt of calcium and magnesium carbonates, $CaMg(CO_3)_2$; containing $CaCO_3$ 54·28, $MgCO_3$ 45·72 p.c., or CaO 30·42, MgO 21·86 p.c. It is a member of the isomorphous series of rhombohedral carbonates (calcite group), and has an angle of 73° 45' between the surfaces of the perfect rhombohedral cleavages. It, however, differs from the other members of the group in the degree of symmetry of its crystals, which are hemihedral with parallel faces. It further differs from calcite in the fact that it never shows lamellar twinning on the obtuse negative rhombohedron. The most usual form of crystal is the primary rhombohedron, the faces of which are parallel to the cleavage directions (this being an unusual form in calcite, except in combination with other forms). The faces are frequently curved, sometimes to such an extent that the crystals are saddle-shaped. The most perfect crystals, such as those found in the crystalline dolomite rock of the Binnenthal

in Switzerland, are colourless and transparent with a vitreous lustre. More often the crystals are white or creamy-white and opaque with a pearly lustre; hence the popular name *pearl-spar*. The mineral is harder (H. 3½–4) and denser (sp.gr. 2·85) than calcite. It may be readily distinguished from the more commonly-occurring calcite by the fact that it is only slightly attacked by cold dilute acid; in hot acid it dissolves with a brisk effervescence. Dolomite is much less soluble in water containing carbon dioxide (3 parts in 10,000 at 18°) than is calcite. Various micro-chemical tests have been devised for the purpose of distinguishing dolomite and calcite, especially in thin sections of rocks. Lemberg's solution contains aluminium chloride and a staining material (haematoxylin or an aniline dye); a stained film of aluminium hydroxide deposits on calcite, but not on dolomite. The composition of dolomite may be varied somewhat by isomorphous replacement. Iron and manganese may replace magnesium, forming a passage through *brown-spar* to ankerite (*q.v.*). Zinc or cobalt is also sometimes present in small amount. Any excess of calcium over the double salt ratio may perhaps to some extent be present in isomorphous mixture, but more often it is probably present as mechanically admixed calcite. Simple ratios of $CaCO_3 : MgCO_3$ other than the 1 : 1 of ' normal dolomite,' probably do not exist. Several trivial names have been applied to varieties of dolomite showing peculiarities of structure or supposed differences in composition; the analyses have not, however, always been made on well-crystallised material.

The best crystallised specimens of dolomite are met with in mineral veins and other metalliferous deposits. For example, with iron ores at Traversella in Piedmont, and Cleator Moor in Cumberland; with lead and zinc ores at Laxey in the Isle of Man, and Joplin in Missouri; with silver ores at Schemnitz in Hungary, and Guanaxuato in Mexico. Crystalline masses occur in serpentine, talc-schist, and other magnesian silicate rocks. As a rule, only quite small crystals are found in dolomite rocks, but occasionally good crystals are found in cavities.

Dolomite rock, dolomitic or magnesian limestone, is, as a rule, more indefinite in its characters and composition, since here the dolomite mineral is mixed with other mineral substances, such as calcite, carbonates of iron and manganese, oxide and hydroxides of iron, argillaceous matter, quartz, etc. With increasing calcite the rock may pass into ordinary limestone; and some authors restrict the term ' magnesian limestone ' to rocks intermediate between ' normal dolomite ' and ordinary limestone. The presence of calcite in a magnesian limestone containing a molecular excess of calcium over magnesium may be demonstrated by etching a polished surface or a thin section with cold dilute acid, when the calcite will be readily dissolved out leaving pits; or by means of the staining test with Lemberg's solution mentioned above.

The purest dolomite rocks are the snow-white crystalline dolomite marbles of the Swiss Alps, Norway, &c., which have sometimes the character of a statuary marble and can be used for ornamental purposes. More often, however, the rock is yellowish, grey, creamy, or brown, and very often cavernous in texture. It is

usually minutely crystalline, consisting of an aggregate of tiny rhombs of dolomite-spar more or less firmly held together, but at times quite loose and sandy. Dolomite rock is of wide distribution and is met with in sedimentary strata of all geological periods. In England a long narrow outcrop extends along the eastern slopes of the Pennines from Nottinghamshire to the Durham coast. This has long been extensively quarried as a building stone, the principal quarries being near Anston in Yorkshire, Bolsover Moor in Derbyshire, and Mansfield Woodhouse in Nottinghamshire. Here the rock is of Permian age. In the Dolomite mountains of southern Tyrol the rock is of Triassic age, whilst that of Swabia belongs to the Jurassic formation.

The origin of dolomite rock has been a subject of much speculation and experimental work of a chemical character. A review is given in Doelter's Handbuch der Mineralchemie, 1912, vol 1. (here also is given a large collection of analyses, methods of analyses, &c.). That of Permian age, which is usually associated with beds of gypsum and rock-salt, is supposed to have been deposited as the double carbonate by chemical precipitation from the salt waters of inland seas. In some other cases the rock has been formed by the action of magnesium-bearing solutions on limestone; either contemporaneously and progressively with the formation of the limestone (as proved by the dolomitisation of coral-limestone—the magnesium in this case being derived from sea-water); or long subsequently by the action of subterranean mineral-waters percolating along the bedding and joint planes (as in the Carboniferous Limestones of Derbyshire and South Wales). Or again, it may have been formed by weathering and the solution of the more soluble calcium carbonate from limestones containing a small proportion of magnesium.

The following are analyses of dolomite rock: I, from Bolsover, Derbyshire; II, Mansfield, Nottinghamshire; III, Anston, Yorkshire; IV, Southern Tyrol —

	I.	II.	III.	IV.
CaO .	28·6	29·0	30·7	31·4
MgO .	19·2	20·4	20·6	19·2
Fe_2O_3, Al_2O_3	1·8	—	0·73	1·2
SiO_2 .	—	3·7	0·56	1·0
CO_2 .	43·5	44·9	46·7	46·1
H_2O .	3·3	2·1	0·75	—

The economic applications of dolomite are confined to the rock, since this is much more plentiful and of wider distribution than the crystallised mineral. Its principal use is as a building stone. For this purpose it is more suitable than ordinary limestone, being harder and more resistant to solvents, but it needs to be carefully selected. It is also used for paving and road-metal. The Houses of Parliament are built of stone from the three English localities noted above (Anal. I.–III). The stones from these quarries have a crushing strength of 484–883 tons per square foot, absorption of 4·6–7·5 p.c., and weigh 134–152 lbs. per cubic foot. Certain varieties of dolomite rock (dolomite marble) find an application as an ornamental stone. Dolomite rock is also extensively used for the basic linings of Bessemer converters and

open-hearth furnaces in the manufacture of steel. For this purpose the rock is calcined until it commences to sinter, crushed, mixed with gas-tar, and moulded in the furnaces or shaped into bricks. The best result is obtained when the rock contains 3–4 p.c. of Fe_2O_3 and Al_2O_3, and about $2\frac{1}{2}$ p.c. of SiO_2. (On British sources of dolomite rock for use as a refractory material, v. Mineral Resources of Great Britain, Mem. Geol. Survey, 1918, vol. vi.) The rock is completely burnt or half burnt below a red heat (giving $MgO+CaCO_3$) for the preparation of cements and plasters; when it contains quite a small amount of argillaceous matter it gives a good hydraulic cement. It is also burnt for agricultural purposes, and is said to be especially beneficial for leguminous crops. It is a readily available source for the manufacture of magnesium compounds, e.g. Epsom salts, magnesium chloride, magnesia alba; but in this direction it was not able to compete with the large quantities of soluble magnesium salts obtained as by-products from the Prussian salt-deposits. Various processes have been suggested for extracting the magnesia for use as a refractory material. In one, the calcined dolomite is mixed with magnesium chloride, forming calcium chloride which is readily removed in solution. In another, the calcined dolomite is treated with a solution of sugar, when the calcium passes into solution as saccharate, from which the sugar can be recovered by precipitating the calcium as carbonate with carbon dioxide. When half burnt to $MgO+CaCO_3$ the magnesia can be extracted by carbonated water under pressure. The pure white dolomite marble is used for the manufacture of pure carbon dioxide for use in the manufacture of aerated waters.   L. J. S.

DOMEYKITE. A copper arsenide, Cu_3As, corresponding to copper 71·7 and arsenic 28·3 p.c. It occurs in reniform, botryoidal, and compact masses, of white or grey colour, with metallic lustre, rapidly tarnishing. H.=3–3·5; sp.gr. 7–7·5. Readily fusible before the blowpipe, with emission of arsenical vapours. Soluble in nitric acid, but not in hydrochloric acid. It is found at Coquimbo and Copiapo in Chile, at Cerro las Paracatas in Mexico, and at Zwickau in Saxony.

Several other arsenides of copper, more or less like domeykite, are known. The *Algodonite* of F. Field is Cu_6As, and occurs at the Algodones mine, near Coquimbo. *Whitneyite*, from Houghton Co., Michigan, U.S., described by F. A. Genth, is Cu_9As; and D. Forbes's *Darwinite*, named after Charles Darwin, is a similar mineral from near Copiapo. *Condurrite*, from Condurrow mine, Cornwall, appears to be a mixture of arsenide of copper with various oxidised products derived from the alteration of tennantite or some kindred species. The names *Keweenawite*, *Mohawkite*, and *Ledouxite* have been applied to various copper arsenides from Michigan, in which the copper is in part replaced by nickel and cobalt.   L. J. S.

DONARITE. An explosive consisting of a mixture of ammonium nitrate (80 pts.), trinitrotoluene (12 pts.), nitroglycerine (3·8 pts.), gun-cotton (0·2 pt.), flour (4 pts.).

DORMIGENE. A urea derivative of α-bromo-isovalerianic acid. Used as a nervous sedative.

DORMIOL. A condensation product of chloral and tertiary amyl alcohol. V. SYNTHETIC DRUGS.

DOSS. Japanese name for a dyewood from an evergreen tree *Ilex Mertensii* (Maxim.), found in the Ogasawara and Okinawa Islands. Contains a dyestuff, *dossetin* $C_{15}H_9O_8$, crystallising in yellow needles; m.p. 271°–272° (Ito, J. Soc. Chem. Ind. 1908, 440).

DOUBLE SCARLET, BRILLIANT SCARLET v. AZO- COLOURING MATTERS. ·

DRACYL. An obsolete synonym for toluene.

DRAGON'S BLOOD. A resin used as a red pigment (v. PIGMENTS; also RESINS).

DRIERS (in the United States also termed 'Japans') is the trade term for those metallic oxides, chiefly oxides of lead, manganese (litharge, red lead, manganese dioxide) and cobalt or their inorganic salts, which were formerly used exclusively in the process of oil boiling as 'driers.' More recently acetate, oxalate, and borate of manganese have been employed. Since metallic salts of linseed oil have the same property, such salts are also manufactured as 'driers.' They are obtained either by precipitating rosin soap solutions with solutions of metallic salts, or by fusing together a metallic oxide with colophony. Hence these are distinguished in commerce as 'precipitated' driers, and 'fused' driers. The latter are readily discriminated from the former by their not containing any moisture. Metallic salts of linseed oil fatty acids are now used as driers; they can be prepared either by precipitation or by the dry process, hence both 'precipitated' manganese linoleate, 'precipitated' lead linoleate, and 'fused' manganese linoleate, &c., are obtainable. The driers prepared from linseed oil fatty acids, as also from rosin (colophony), are soluble in oil of turpentine, ether, chloroform, and linseed oil itself. Hence they are also termed in commerce 'soluble driers.' Solutions of these driers in linseed oil or in turpentine oil, or in a mixture of both, are obtainable in commerce under the name 'liquid driers,' 'terebene,' and other fancy names.

The function of these driers appears to be to absorb oxygen from the air and transfer it to the linseed oil, thus accelerating its drying to a flexible film when exposed to the air. On this assumption, the fact that litharge and manganese dioxide act as driers will be best explained by stating that at the high temperature at which linseed oil is 'boiled,' the oxides saponify the linseed oil, forming therewith lead or manganese soaps, which then act in their turn in the manner indicated above. From experiments on the behaviour of cerium salts obtained from various drying oils, Morrell (Chem. Soc. Trans. 1918, 113, 111) concludes that a change occurs in the intra-molecular linkings when drying oils are polymerised by heat. The action of cerium α-oleostearate (from tung oil) as a drier may be represented by the following scheme:—

$$CeX_3 \text{ or } CeOX_6 \rightarrow Ce_2(XO_2)_6$$
$$CeO(XO_3)_6 + \text{drying oil}$$
$$\rightarrow CeX_3 + O\cdot CHY$$
$$| \quad \text{[oxidised oil]}$$
$$O\cdot CHZ$$

This representation is also in accord with the

conclusions of Ingle (J. Soc. Chem. Ind., 1917, 318) as to the behaviour of lead linolenate. Cerium driers are less effective than cobalt or manganese linoleate in accelerating the drying of a varnish containing a lead drier. The following are the analytical data obtained by the author in the examination of a drier :—

				Per cent.
Ash	.	.	.	18·6
Fatty and rosin acids	.	.	83·4

The more detailed examination gave the following result :—

				Per cent.
Lead oxide	.	.	.	10·99
Manganous oxide	.	.	6·79
Iron peroxide	.	.	.	0·47
Calcium oxide	.	.	.	0·56
Rosin acids	.	.	.	38·32
Oxidised acids	.	.	4 24
Other fatty acids	.	.	40·86

It should, however, be understood that the results furnished by chemical analysis alone are not sufficient to supply the data on which to base an opinion as to the properties which a drier will impart to the oil The colour and drying power of the boiled oil to be prepared and other conditions greatly influence the choice and the quantity of a drier to be employed on a large scale. J. L.

DROP GUM or **GAMBOGE** v. PIGMENTS.

DROSERA WHITTAKERI. *Drosera whit-takeri* is found in Australia, and grows plentifully on the hills near Adelaide. The tuber of this plant consists of an inner solid but soft nucleus full of reddish sap or juice, and an outer series of easily detached thin, and more or less dry, layers of an almost black material. Between these layers are to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants (Rennie, Chem Soc. Trans , 1887, 51, 371 ; 1893, 63, 1083).

The colouring matter is extracted from the tubers by means of hot alcohol, the solution evaporated, and the residue, containing a little alcohol, is then mixed with water and allowed to stand. The product is dried, sublimed, and the brilliant vermilion powder, which contains two substances, is fractionally crystallised from boiling alcohol, or acetic acid.

The •more sparingly soluble compound $C_{11}H_8O_5$ forms red plates, melts at 192°-193°, dissolves in alkaline solutions with a deep red violet colour, and gives a *triacetyl derivative*, $C_{11}H_5O_5(C_2H_3O)_3$, melting-point 153°-154°.

The *monosodium* compound $C_{11}H_7O_5Na,2H_2O$, gives dark reddish-brown needles, the *disodium* compound $C_{11}H_6O_5Na_22H_2O$, brown needles, and the *calcium* compound $(C_{11}H_7O_5)_2Ca,3H_2O$, dark brown crystals.

By treatment with stannous chloride or hydrochloric acid, this substance $C_{11}H_8O_5$ yields a reduction product $C_{11}H_{10}O_5$, yellow needles, melting-point 215°-217°. When dry, this is stable in air, but if left in contact with alcohol or water, it soon becomes red owing to oxidation. According to Rennie it is probable that the original colouring matter is a *trihydroxymethyl-naphthoquinone*, in which case the substance $C_{11}H_{10}O_5$ will consist of the corresponding

hydroquinone derivative. The more readily soluble compound contained in the tubers possesses the formula $C_{11}H_8O_4$. It crystallises in red needles, melting-point 174°-175°; dissolves in alkaline solutions with a deep-red colouration; and gives a *diacetyl* derivative, $C_{11}H_6O_4(C_2H_3O)_2$, yellow needles, melting-point 107°-110°. A. G. P.

DRUMINE. An alkaloid stated to be present in *Euphorbia Drummondii* (Ogston, Brit. Med. Jour. 1887, 451).

DRY CLEANING. French or chemical cleaning, *Nettoyage à Sec*. A process of removing dirt, grease, &c., from fabrics by solvents other than water, such as petroleum benzine, coal-tar benzene, carbon tetrachloride, &c. The substitution of such liquids for water seems to have been first made in France during the middle of the last century by the application of ' camphene,' a terpene used at that period for illuminating purposes.

The process was introduced into the United Kingdom, in 1866, by Messrs. Pullar & Sons, who greatly developed it, employing machinery to a large extent in place of the hand labour formerly used.

The solvents mainly used at the present time are ' benzines,' usually obtained from American and Borneo petroleum, of sp.gr. 0·78 ; boiling between 80° and 120°. The benzols employed are what are known commercially as 90's and 50's. They may contain sensible quantities of carbon disulphide, thiophen, and possibly other sulphur products, which are apt to impart a disagreeable smell to the fabric. Carbon tetrachloride, on account of its relatively high price, is only used to a limited extent. It has the great advantage over the hydrocarbons that it is uninflammable, and can be employed in particular cases where the use either of benzine or of benzol is inadmissible. (For a method of valuing benzine for the purpose of the dry cleaner, v. Trotman, J. Soc. Chem. Ind. 1906.)

Thiophen in benzol may be detected by the isatin and sulphuric acid reaction (v. THIOPHEN). (*Cf.* Schwalbe, Chem. Zeit. 1905.)

Carbon disulphide may be detected by the formation of a precipitate with phenylhydrazine, and determined quantitatively by conversion into potassium xanthate by means of alcoholic potash (v. CARBON DISULPHIDE).

An admixture of paraffin hydrocarbons with the benzol may be recognised by nitrating the sample with nitrosulphuric acid and subsequent steam distillation. •

The carbon tetrachloride employed for degreasing should be free from hydrochloric acid or traces of free chlorine. It should also contain no chloroform or phosgene gas, which are apt to act deleteriously upon the workpeople.

Special soaps, soluble in benzine, are employed in dry cleaning. They not only assist the degreasing, but diminish the risk of fire. The soaps consist of practically anhydrous oleates or stearates of potash or soda made by melting together oleic acid and soap, or by dissolving the alkali in methylated spirit, and adding to the solution the requisite quantity of oleic acid or melted stearic acid. Strong ammonia solution may be employed instead of potash or soda. •

(For a description of the methods and

machinery employed in modern processes of dry cleaning, and of the apparatus for the recovery and purification of the solvents used, v. Dyeing and Cleaning, by F. J. Farrell, Griffin & Co., Ltd. 1910.)

DULCAMARA. *Bittersweet, Woody night-shade.* (*Douce amère*, Fr. ; *Bittersuss*, Ger.) The young branches of the *Solanum dulcamara* (Linn.), were formerly administered as a decoction in rheumatism and skin diseases. They contain an amorphous glucoside *dulcamarin* $C_{22}H_{34}O_{10}$ (Geissler, Arch. Pharm. [iii.] 6, 1010) ; and *solanine* $C_{42}H_{75}O_{12}N$, m.p. 235° ; *solanidine* $C_{41}H_{71}O_2N$, m.p. 205° ; and *solaneine* $C_{48}H_{78}O_{13}N$ (Davis, Pharm. Y. [iv.] 15, 160). G. B.

DULCIN. *p*-Phenetol-carbamide

$$C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$$

A sweet substance. Used as a substitute for saccharin.

DULCITOL *v.* CARBOHYDRATES.

DUMASIN. Pentamone. *v.* KETONES.

DUNGING SALT. *Sodium Arsenate v.* ARSENIC.

DUOTAL. Guaiacol carbonate
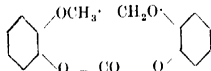
formed by the action of phosgene gas on an alkaline solution of guaiacol. Used in the treatment of phthisis.

DURA or **DARI.** A grain imported from India and the Sudan, chiefly as a poultry food. Composition : moisture, 8·45 ; proteins, 12·98 ; other nitrogenous substance, 0·08 ; fat, 3·30 , starch, 62·66 ; other carbohydrates, 9·74 ; fibre, 1·03, ash, 1·71 p.c. ; food units 113·3 ; nutrient ratio, 1 : 6·1. Contains no alkaloids or cyanogenetic glucosides (Bull. Imp. Inst 1913, 11, 33) For the use of Sudan Dura as a brewing material, *see* Briant & Harman, Journ. Instit. Brewing, 1918, 209.

DURENE *v.* CYMENES.

DURENOL *v.* PHENOL AND ITS HOMOLOGUES.

DUTCH PINK or **ITALIAN PINK** *v.* PIGMENTS.

DUTCH ULTRAMARINE. *Cobalt blue v.* COBALT AND PIGMENTS.

DURINE. A preparation of formaldehyde.

DYEING. The art of dyeing consists in imparting colour to the substance of various materials, usually textile fabrics, in such a manner that it is not readily removed or altered by those influences to which the dyed material is subsequently exposed. *Tinting* is essentially the same as dyeing, but the term is applied to the production of light shades only. In *staining*, the colour is not so permanently fixed as in dyeing, but in all these processes the colouring substance is presented to the material in a dissolved condition. In textile *printing*, the colour is applied to portions of the material only, thus producing a pattern, but in other respects, many printing operations are, in principle, similar to dyeing. In some processes of textile printing, as in *painting*, on the other hand, a more or less opaque pigment is applied to the surface of the material by means of adhesives, thus partially or entirely obscuring the true surface.

Dyeing is of chief importance in connection with the textile industries, but many other materials are coloured by dyeing processes, such, for example, as leather, feathers, horn, ivory, bone, straw, and wood.

The various materials above enumerated show remarkable differences in behaviour towards any particular dyestuff. Wool, silk, leather, feathers, horn, and animal skin products in general, behave somewhat similarly towards colouring matters, but the dyeing properties of cotton, linen, and other vegetable products are quite different.

Differences quite as marked are to be noted in the behaviour of various colouring matters towards one and the same material, and thus, in dyeing operations, both the nature of the material to be dyed and of the colouring matter employed, have to be taken into account.

The theory of dyeing. The precise cause or causes of the different behaviour of the textile fibres in dyeing is still a matter of uncertainty ; but there is little doubt that the chemical and physical properties both of the fibre and of the dyestuff are all factors of the complicated phenomena of dyeing.

The earliest theory with regard to the fixation of dyes was that the action is purely mechanical, and it is still urged by many that rarely in dyeing processes is there direct evidence of chemical combination between fibre and dyestuff Both bodies, as a rule, retain their individual chemical and physical properties unchanged, and the dye can frequently be removed from a fibre by means of alcohol or another solvent.

In its earliest form, the mechanical theory was put forward by Hellot and d'Apligny in 1780. (See Hellot's L'Art de la Teinture des Laines (1734) ; and d'Apligny's L'Art de la Teinture des fils de Coton (1776).) They assumed that the particles of colouring matter became embedded in the minute pores permeating the fibre substance. Crum (Chem. Soc. Trans. 16, 404) strongly supported this theory, while Muller-Jacobs (J. Soc. Dyers, 1885, 63) expressed much the same idea in attributing the fixation of dyes to membranous diffusion. It has, however, been shown by several investigators that dyeing processes do not obey the general laws of osmosis. v. Georgievics (J. Soc. Chem. Ind. 1895 149) considers dyeing is chiefly due to surface attraction. Witt (Farber-Zeit. 1890) put forward a modification of the mechanical theory. He regards the fibres as solid solvents in which the dyestuffs dissolve, the latter being withdrawn from its aqueous solution in the same way as, *e.g.* ether will extract many substances from their aqueous solution. The degree to which a dye-bath can be exhausted will then depend upon the relative solubility of the dyestuff in the acid or neutral dye liquor and in the fibre substance under the conditions (concentration and temperature) used. Krafft (Ber. 1899, 1608) attributes dyeing phenomena to a separation of the dyestuff upon the fibre in a colloidal state, and this view has been supported by Biltz (*ibid.* 1904, 1766), Linder and Picton (Chem. Soc. Trans. 1905, 1931), and Dreaper (J. Soc. Chem. Ind. 1905, 223).

The chemical theory of dyeing was originally put forward by Macquer and Bergman in opposition to the mechanical theory of Hellot and d'Apligny, and has received much experimental

support from Persoz, Berthollet, Chevreul, Kühlmann, Vignon, Knecht, and many others. It is mainly based on the following facts : wool and silk fibres contain amino-acids, and thus possess strongly marked acidic and basic functions. Cellulose, the essential constituent of the vegetable fibres, is chemically much less active, and dyes much less readily than wool and silk, but under certain conditions it exhibits weakly acidic functions. All dyestuffs (with few exceptions) possess either acidic or basic properties, or are in the form of salts, which dissociate in the dye-bath ; and chemical combination between fibre and dyestuff would thus, *primá facie*, be expected. Moreover, *lanuginic* and *sericinic acids*, which are produced respectively by the hydrolysis of wool and silk, precipitate both acid and basic dyes from their aqueous solution (Knecht and Appleyard, J. Soc. Dyers, 1889, 72).

A full discussion of the evidence for and against the mechanical and chemical theories of dyeing cannot be here entered upon, but a general review indicates that the attempt to cover all dyeing phenomena by any one simple explanation must fail, and that many factors are concerned, the relative importance of which varies in different cases. In the dyeing of wool or silk, with acid or basic dyes, it may be taken as established that chemical combination occurs, but prior to this some hydrolysis of the fibre, and more or less complete ionisation of the dye-stuff takes place. Surface concentration of the dye on the fibre probably also occurs, and the coagulation and precipitation of the dissociated colloidal dyestuff also plays a part. This is supported by the observation that the temperature of maximum *absorption* of dye does not (in the cases investigated) correspond with that of maximum *fixation* (Dreaper, Trans. Faraday Soc. 1910, pt. i. Haldane-Gee and Harrison, *ibid.*) ; the former possibly coinciding with the point of maximum coagulation and precipitation, and the latter indicating the point of maximum degree of chemical combination. Whether the superficially precipitated dye penetrates the fibre by osmosis or by 'solid solution' is mainly a question of definition of terms.

In the case of the dyeing of vegetable fibres, the same factors probably operate, but their relative importance is not the same, the physical factors—precipitation, surface attraction, and osmosis—predominating over the effect of direct chemical action.

Classification of colouring matters. It has already been pointed out that dyestuffs vary in their behaviour. If, *e.g.* separate pieces of wool are boiled in solutions containing, (*a*) logwood, (*b*) indigo, (*c*) magenta, and (*d*) picric acid, the following results are obtained : (*a*) the wool acquires a brown stain ; (*b*) the wool remains undyed, the indigo floating about in an insoluble condition ; (*c*) the wool is dyed a magenta colour ; and (*d*) the wool is dyed a full yellow. If the experiment is repeated on wool which has been previously boiled with a solution of potassium dichromate, the result will be that in (*a*) the wool is dyed black, whereas in (*b*), (*c*), and (*d*), similar results are obtained to those of the previous experiments. Logwood, therefore, must be applied in conjunction with potassium dichromate or some similar substance, *i.e.* with a mordant ; whereas magenta and picric

acid dye without such aid, and indigo requires a special process, the nature of which is not indicated by the results of the above-described experiments.

Colouring matters may be divided into three groups on the lines indicated above, viz. : (1) those which must be applied in conjunction with a mordant ; (2) those which dye direct from their solutions ; and (3) those requiring special processes.

As regards groups (1) and (2) this classification is practically identical with that of Bancroft (Philosophy of Permanent Colours, i. 118, London. 1794), who, upwards of a hundred years ago, divided colouring matters into *substantive dyes* and *adjective dyes* ; the former class comprising those which dye directly from their solutions, and the latter being composed of those dyes which require mordants. Nietski (Farber-Zeit. 1889–90, 8) uses the terms *direct dyes* and *mordant dyes* in exactly the same sense, and both Bancroft's and Nietski's terms are still in use. Hummel (The Dyeing of Textile Fabrics, 1st ed. 1885, 147) also classifies dyestuffs into two groups ; *monogenetic dyes* being such as are capable of producing one colour only, while *polygenetic dyes* produce distinct colours with different mordants. The members of the first group are *coloured bodies*, and these merely require to be fixed upon the fibre, whereas the *colouring principles* comprising the second group as a rule only develop a colour when chemically combined with a mordant.

It will be seen that these three systems of classification closely correspond, the terms *substantive dyes, direct dyes*, and *monogenetic dyes* being almost synonymous, as are *adjective dyes, mordant dyes*, and *polygenetic dyes*. It should, however, be pointed out that none of these classifications is absolute ; magenta, for example, is a direct dye as applied to wool, but requires a mordant when used for cotton.

A distinct method of grouping dyestuffs is that of Benedikt (The Chemistry of the Coal-tar Colours, 1886, 29), who distinguishes between *colour acids, colour bases*, and *neutral colouring matters*. Both colour acids and colour bases are fixed on the fibre in the form of salts, but whereas in the colour acids the essential colour-producing group resides in the acid portion of the compound, in the colour bases the reverse is the case. Alizarin red, dyed on wool, is a salt of which alumina forms the basic and alizarin the acidic constituent. Alizarin is therefore a *colour acid.* Similarly, the red pigment formed on dyeing tannin-mordanted cotton with magenta is a combination of rosaniline base with tannic acid. Magenta is therefore a *colour base.* Indigo and other vat dyes are *neutral colouring matters.*

All the above schemes of classification are defective, either from the point of view of the practical dyer, or the chemist. As regards practical application, the large number of dyestuffs now on the market may, however, be satisfactorily classified into the following groups : (1) *mordant dyes* ; (2) *acid-mordant dyes* ; (3) *acid dyes* ; (4) *direct dyes* ; (5) *basic dyes* ; (6) *sulphide dyes* ; (7) *vat dyes* ; (8) *ingrain dyes.*

The classification of dyes according to chemical constitution is based upon the existence,

of a certain group of atoms, in all members of each class, upon the integrity of which their colouring power depends. This is termed the *chromophorous group*, the theory being first put forward by O. N. Witt, in 1876. The introduction of such a chromophor into a suitable colourless compound is accompanied by the development of colour, *e.g. benzene* (C_6H_6) is colourless, but *azobenzene* ($C_6H_5-N=N-C_6H_5$) is orange-coloured. Many substances, however, such as azobenzene, although strongly coloured, are devoid of dyeing power. Such bodies are termed *chromogens*, and in order to convert them into useful dyes, the introduction of a salt-forming group is necessary ; such groups, in this connection, being termed *auxochromous groups*. Thus, whilst *azobenzene* is not a dye-stuff, both *amino-azobenzene* and *hydroxy-azobenzene* are useful dyes. In these compounds, the azo- group ($-N=N-$) is the *chromophor*, and the amino- or hydroxyl- group is the *auxochrome*.

The presence of both a chromophor and an auxochrome does not, however, necessarily indicate that a substance is a useful dye. For example, *trinitroaniline*, $C_6H_2(NO_2)_3NH_2$, contains the chromophor (NO_2) and the salt-forming auxochrome group (NH_2) ; but it is not a useful dyestuff, because the basic character of the auxochrome is neutralised by the strongly acidic chromophor. On the other hand, trinitrophenol $C_6H_2(NO_2)_3OH$ is the useful dyestuff picric acid.

Those dyestuffs which do not contain a salt-forming auxochrome cannot be applied by ordinary dyeing processes, and the fact that a special process is required, *e.g.* for indigo, is not primarily due to its insolubility, but to its neutral character.

The scheme of classification, based on the chromophor, distinguishes the following groups—

Group	Chromophor	Typical dyes
1. *iso*-Nitroso- or oxime	$>C-O$ $>C-N'OH$	Resorcin green, dioxine, gambine.
2. Nitro-	$-NO_2$	Picric acid, naphthol yellow.
3. Azo-	$-N=N-$	(a) *Basic*—chrysoidine, Bismarck brown, Janus red (b) *Acid*—azo- oranges and scarlets, naphthol black, diamond black. (c) *Direct*— benzopurpurin, diamine colours, direct blacks (d) *Mordant*—'acid mordant' or 'chrome' colours
4. Triphenyl-methane,	(ring)	Magenta, methyl violet, Victoria blue, *patent blue, malachite green.
5. Oxyketone	CO (ring) CO	The alizarin dyes, indanthrene and algol vat dyes.
6. Pyrone	$-O-$ $-C=$	Rhodamine, violamine, eosins.
7. Acridine	$<$N$>$C$>$	Acridine yellow, orange, and scarlet.
8. Oxazine	$<$O$>$N$>$	Meldola's blue, gallocyanin, Capri blue.
9. Thiazine	$<$S$>$N$>$	Methylene blue, thiocarmine, hydron blue.

Group	Chromophor	Typical dyes
10. Azines	(N ring) or $<$N$>$N$>$	Safranines, indulines, aniline black.
11. Thiazol-	$-S$ $-N$$>C-$	Primuline, thioflavin.
12. Quinoline	$-CH-CH$ N_2CH	Quinoline yellow, cyanine.
13. Flavone	$-O-C-$ $-CO-CH$	Fustic, weld, logwood, Brazil wood.
14. Indigoids	$-CO-C=C-CO$	Indigo, helindone and ciba vat dyes.
15. Miscellaneous.		

This classification of dyestuffs into chemical groups is of importance in the identification and testing of dyestuffs, as the constitution of the compound determines its behaviour towards reagents. It is not, however, a convenient one as regards the practical application of the dyestuffs.

Essential properties of a dyestuff. In order to rank as a useful dye, a substance must possess certain essential features. A *direct dye* must not only possess a colour of considerable intensity and permanence, but must also be capable of easy fixation on textile fibres without injury to fibre or dyestuff. For example, both vermilion and azo-scarlet possess a brilliant colour, but the former is not a dyestuff, because it cannot be applied or produced by dyeing processes. A *mordant dye*, on the other hand, need not possess a strong colour, and may, in fact, be colourless. It must, however, be capable of producing strongly coloured and insoluble colour-lakes in combination with suitable mordants. *Vat dyes—e.g.* indigo—are, as a rule, quite insoluble in water, and therefore cannot be applied by an ordinary process. The essential feature of this group is that their reduction products are soluble in alkaline solutions, and on this fact the method of application depends.

In order to constitute a dyestuff a body must, therefore, either be strongly coloured in itself or be capable of producing coloured lakes. It must also be of such a character that it can be fixed upon textile material from an aqueous solution, and it must produce a colour which possesses sufficient permanence and resistance to washing and other influences. (In so-called 'dry dying' alcohol or other volatile solvent is used)

Operations preliminary to dyeing processes. In any dyeing operation, the chief bodies concerned are the fibre to be dyed and the dyestuff. In their natural condition, all textile fibres contain impurities which not only detract from their appearance, but prevent their being satisfactorily dyed. The removal of these impurities is the object of the washing, scouring, and bleaching processes which the ' raw ' fibres undergo.

A great bulk of manufactured textile material, chiefly cotton and linen, is used in the undyed condition, but wool and silk are usually dyed.

Dyeing processes. Dyeing may take place at various stages of the manufacture of textiles. ' *Piece dyeing* ' is generally employed when a plain-coloured material is required, being the most economical and convenient process. If a coloured pattern is required, the material must either be printed, or dyed before weaving, and

the process may then be carried out on the raw wool or cotton ('*wool dyeing*,' '*cotton dyeing*'), at an intermediate process ('*sliver*' or '*slubbing dyeing*') or upon the spun yarn ('*yarn dyeing*,' '*hank dyeing*,' '*cop dyeing*,' '*cheese dyeing*,' '*warp dyeing*').

Wool is dyed in all these forms; silk, almost exclusively in the form of yarn; and cotton, chiefly as warps, cops, or pieces.

The dyeing of wool. Wool may be dyed with a greater range of colouring matters than any other textile fibre. All the various classes of colouring matters enumerated in the classification based on practical application (*see* p. 575) are used in the dyeing of wool; the most important groups being the *mordant*, the *acid mordant*, the *acid* and the *direct* dyes, as well as the *vat dye*, indigo. In boiling solutions, the affinity of wool for dyestuffs is generally greater than that of silk, but at temperatures below 60° the relative affinity is frequently reversed. By a suitable selection of dyestuffs and control of the process, it is therefore possible to dye the wool and silk in a woven fabric either to different shades, or to produce a uniform colour on the two fibres. As a general rule, dyeing processes which produce good results on wool are entirely unsuited for cotton, and it is an easy matter to dye one of the two fibres when present in a mixed fabric and leave the other practically unstained. If both fibres are to be dyed the same or different colours, two distinct processes are, as a rule, required.

Different varieties of wool behave differently in dyeing, the finer wools, such as merino, requiring a larger amount of dyestuff to produce a given shade than the coarser qualities, *e.g.* Lincoln or '*crossbred*' wool. The absorption of dye is, however, by no means entirely governed by the diameter of the fibre, *e.g.* fine silky mohair is very difficult to dye, probably on account of the close texture of the external scales. Fibres taken from different portions of the same fleece also vary somewhat in dyeing properties; and wool taken from the skin of animals slaughtered for meat, or from diseased animals, also differs from '*fleece*' wool as regards its affinity for dyes. All these differences are shown to a much greater extent with some dyestuffs than with others.

The affinity of wool for certain dyestuffs may be increased by suitable treatment with acids, alkalis, or oxidising agents (bleaching powder or hydrogen peroxide solution), or may be diminished by a treatment with tannic acid solution and in other ways. Various colours may thus be produced by a '*piece-dyeing*' process by weaving together untreated wool and wool treated with one or other of the above-mentioned reagents.

The behaviour of wool towards solutions of metallic salts governs the use of these bodies as mordants. When boiled in solutions of salts of the heavy metals having an acid character (*e.g.* sodium dichromate), a decomposition of the salt takes place, and an insoluble basic salt or a hydrated oxide is fixed upon the fibre.

The dyeing of silk. In general behaviour towards colouring matters, silk resembles wool, but, as a rule, dyes are fixed on silk in a less permanent manner than on wool. The dyeing of silk appears to depend, to a greater extent, on absorption, and to a less extent on chemical action. The *acid*, *basic*, and *direct* dyes are

chiefly used on silk, but other classes, *e.g.* the *mordant* and *vat* dyes, are also employed, though they tend to detract somewhat from the brilliant lustre and suppleness on which the beauty of silk depends. The maximum absorption of dyes by silk usually takes place at 60°–80°, and not at 100° as in the case of wool.

The so-called '*dry dyeing*' process sometimes employed for silk consists in the use of benzine or other volatile liquid as a solvent for the colouring matter in place of water. The usual dyestuff-salts are not soluble in benzine, but the fatty acid compounds or resinates of basic dyes are readily soluble.

The mordanting of silk with metallic salts is usually carried out in cold concentrated solutions of basic salts, chiefly basic aluminium sulphate for colours, and basic ferric sulphate or ferrous acetate for blacks.

The production of black upon silk is a matter of great importance, and is almost a trade to itself. The silk is first immersed in a solution of chestnut extract or other tannin matter, and then in a solution of basic ferrous acetate (pyrolignite of iron) or ferric sulphate ('nitrate of iron'). By successive alternate treatments in these liquors, the silk may be weighted to the extent of 400 p.c. It is then dyed with logwood extract. There are a number of alternative processes for the black dyeing of silk.

Wild silks, of which *Tussur* is the chief variety, are much more difficult to dye than ordinary silk, the fine fibrillæ of which the fibre is composed being very impervious. The bandlike flat surface of the fibre also reflects the light in such a manner that a white shiny appearance is liable to be produced instead of a rich, intense colour or black

Artificial silks, consisting essentially of cellulose, are more allied to cotton than to silk as regards dyeing properties. Those varieties produced from collodion (Chardonnet silk) dye more readily with the basic dyes than do cotton or the artificial silks obtained from a cuprammonium solution of cellulose (Pauly, Lehne, Thiele or 'glanzstofle' silk) or from cellulose xanthate ('viscose silk'). There is, however, much individuality in the dyeing properties of the various forms of artificial silk.

The dyeing of cotton. Cotton is dyed chiefly in the form of hanks or warps, less frequently as loose cotton or piece goods. The dyeing of cotton on the spool, cop or beam is, however, now of great importance.

The dyeing properties of cotton differ greatly from those of wool, and therefore the processes and materials used also differ. Until the discovery of Congo red in 1884, there were three dyestuffs only which were capable of dyeing cotton directly from their aqueous solution—*turmeric*, *safflower*, and *annatto*—but there are now a large number of synthetic substantive dyes by means of which any desired shade can be obtained. The very numerous class of *acid dyes* which are of such great importance in wool and silk dyeing do not produce reasonably fast colours on cotton.

Cotton has no affinity for metallic salts, and therefore does not become mordanted by boiling in their solutions. Indirect methods have therefore to be adopted in applying the

basic mordants required for the fixation of the mordant dyestuffs on cotton. This fibre exhibits a remarkable affinity for tannic acid, which is withdrawn from dilute solution and concentrated on the fibre to a considerable extent. The tannic acid may then serve for the fixation either of metallic mordants or of basic dyestuffs upon the fibre.

The *vat dyes* and sulphide dyes are now of first importance, since, by their use, extremely fast colours are obtained upon cotton.

The so-called *ingrain dyes* are used almost exclusively on cotton. The term is applied to designate a class of dyes which are produced *in situ* on the fibre by precipitation.

Mercerised cotton is virtually a distinct textile fibre, and whilst its dyeing properties are essentially the same as those of ordinary cotton, its treatment requires special precautions on account of its great affinity for the direct dyes.

The dyeing of linen. The behaviour of linen towards the respective classes of dyestuffs is similar to that of cotton, but it is more difficult to dye. The inferior dyeing affinity of linen is probably due to the different physical structure of the fibre.

The dyeing of jute. Although a cellulose derivative, jute differs from cotton and linen, both in its chemical composition and properties. As regards dyeing processes, it behaves, to a certain extent, like tannin-mordanted cotton, and may be dyed not only with *direct*, but with *basic* colouring matters without the aid of a mordant.

The dyeing of leather. Leather resembles wool in dyeing properties, but the difficulty of dyeing it in fast colours is increased by the necessity of using lukewarm liquors only, since boiling water destroys ordinary leather. Certain of the newer methods of producing leather, *e g* chrome tannage, yield a product which will withstand boiling solutions. It is very important as regards the permanence of the leather (when used *e.g* for bookbinding or furniture covering) that no mineral acid should be employed in the dyeing process. As a substitute, formic acid may be recommended. The *acid* and *basic* colouring matters are chiefly employed, the *mordant* dyes being used to a less extent.

The dyeing of feathers. The chief cause of difficulty in the dyeing of feathers is their natural water-resisting property. This is due partially to their ultimate physical structure, and partially to the natural grease present. The midrib is specially difficult to dye. Apart from these special difficulties, feathers behave in dyeing, like wool, and may be dyed with *acid*, *basic*, *direct*, or *mordant* dyes. Reds, browns, blues, and other colours are usually dyed with acid dyes, but the most satisfactory blacks are obtained by successive and repeated treatments with logwood extract, and ferrous sulphate with potassium binoxalate. Dyeing must proceed for a considerable period at the boil, in order to ensure penetration.

The dyeing of horn. Horn is dyed in strong solutions of *acid* dyes by steeping for a long period in the cold or slightly warm baths, which are acidified with acetic or formic acid. Since it contains sulphur, horn may be dyed brown by steeping in a solution of sodium plumbite, which results in the formation of lead sulphide. Black is also produced by alternate steepings in solutions of mercuric nitrate and potassium sulphide.

The dyeing of ivory. Both *acid* and *basic* dyes may be employed in the dyeing of ivory, the former being used with addition of acetic or formic acid in hot solutions. Alcoholic solutions of colouring matters may also be employed. Red is frequently dyed by the cochineal single-bath process used for wool (see p. 590).

Black is produced either by the logwood and iron or aniline black process, as used in cotton dyeing, or by means of silver nitrate.

The dyeing of wood. The method of dyeing wood in bulk is to boil or steam it to remove the resins, and then treat it in an apparatus similar to that employed in creosoting. The wood is placed in a closed vessel which is exhausted by a vacuum pump, and when the air has been sucked out from the pores as completely as possible, the hot dye liquor is admitted into the vessel and put under pressure by a force pump. The direct and basic dyes may be employed Wood is usually dyed black by alternate treatments with logwood extract and sodium dichromate solution.

The dyeing of straw. Straw is largely dyed for use in the manufacture of hats and baskets. There are two commercial varieties, distinguished as *chip* and *straw*. Chip is readily dyed by means of the *direct cotton dyes* of the *sulphide dyes*, and many *basic* and *acid dyes* in neutral solution may also be employed. The process must be continued for 2 to 3 hours at the boil.

'Straw' is more difficult to dye than 'chip,' on account of the highly siliceous character of the surface. The straw should be steeped for several hours in warm water before dyeing. Blacks are usually obtained with logwood and iron, but for colours the *direct cotton* and the *basic dyes* are chiefly used.

MATERIALS USED IN DYEING OPERATIONS.

A great variety of chemical substances are used in dyeing processes—acids, alkalis, oxidising and reducing agents, metallic salts, and a wide range of organic bodies. Two groups only need be here considered, viz. : (*a*) *mordants*, and (*b*) *colouring matters*.

Mordants. The function of a mordant is to chemically combine with the dyestuff employed, and fix the latter upon the fibre. It has already been mentioned that many colouring matters do not require the aid of mordants, but dye direct from their solutions. This applies to the *acid*, *direct*, *basic*, and *vat* dyes when used for wool and silk, and the *direct*, *sulphide*, and *vat* dyes when used for cotton. On the other hand, the *mordant* and *acid-mordant* dyes (as their name implies) demand the use of mordants on wool, as do the *mordant* and the *basic dyes* on cotton.

It is evident that the chemical properties of the dyestuff will govern the character of the mordant required for its fixation, and two types of mordants may thus be distinguished : (1) the *metallic* or *basic mordants*, used for the *mordant' dyes* ; and (2) the *acid mordants*, required in applying the *basic dyes* to cotton or other vegetable fibre.

Basic mordants are employed for fixing on

animal and vegetable fibres those colouring matters which are of an acidic character, *i.e.* either true acids or bodies containing hydroxyl-groups, of which the hydrogen is replaceable by metals. They are metallic salts, of which the most important are certain compounds of chromium, aluminium, iron, and tin.

Wool is mordanted by boiling it with dilute solutions of these metallic salts, usually with the addition of certain acids or acid salts, *e.g.* cream of tartar, sulphuric acid, formic acid, oxalic acid, &c. During this operation, the wool assists in the dissociation of the metallic salt; an insoluble basic salt being fixed within and upon the fibre, while a more acid salt remains in solution. The acids or acid salts, which are added along with the metallic salt, possibly assist the dissociation of the latter by forming more sensitive salts (tartrates, oxalates, &c), and are conveniently termed *assistants*.

As a rule, the mordanting operation precedes that of dyeing, not infrequently, however, the two operations take place simultaneously, and the dyeing is thus effected by the so-called 'single-bath' or 'one-dip' method, as, for example, in producing cochineal scarlet on wool In such cases, the wool is boiled in a solution containing colouring matter, metallic salt, and assistant, in certain accurately determined relative proportions. Combination takes place between the colouring matter and the mordant, but the pigment which would otherwise be precipitated, is retained in solution by the liberated acid of the mordant or the assistant present, and is only gradually withdrawn from solution by the fibre, which thus becomes dyed.

In the case of the 'acid-mordant' dye-stuffs, the application of the mordant follows that of the colouring matter.

Silk may be mordanted in the same manner as wool, by boiling with metallic salt solutions; but, more usually, it is steeped for about 12 hours in cold solutions of the mordants previously rendered more or less basic and sensitive. By subsequently washing with (calcareous) water, the metallic salt absorbed by the silk is dissociated, and an insoluble basic salt is precipitated within the fibre.

Cotton is mordanted with metallic salts by processes very different from those adopted for wool and silk, since it has not the property of causing the dissociation of the metallic salts when boiled or steeped in their solutions. The methods adopted also vary according to the form of the material, *i.e.* whether it be cotton-wool, yarn, or cloth.

With calico, it is usual to impregnate the fabric with solutions of metallic *acetates*, then to dry it, and expose for several hours to a moist warm atmosphere. During this so-called 'ageing' process, dissociation of the salt takes place, acetic acid escapes, and a more or less basic salt remains fixed upon the fibre.

Sometimes the 'ageing' is replaced by a 'steaming process,' in which the fabric is exposed from ½ to 1 hour to the action of high or low pressure steam in a closed chamber. This method is adopted by the printer of textile fabrics in the so-called 'steam style,' in which a mixture of colouring matter and metallic salt (usually acetate) is printed upon the fabric, which is then dried and steamed. The metallic salt is decom-

posed, a basic salt is precipitated upon the fibre, and at the same time the mordant combines with the colouring matter and produces the coloured pigment. This method is analogous to the single-bath process of the woollen dyer.

Cotton may also be mordanted by impregnating it with a metallic salt solution, drying, and then passing through a solution of an alkaline substance, *e.g.* ammonia, chalk, sodium carbonate, &c., to neutralise the acid and precipitate upon the fibre a basic salt or metallic oxide. Solutions of an alkali salt, the acid of which forms an insoluble compound with the base of the mordant, *e.g.* sodium phosphate, silicate, arsenate, &c., are also employed. The substances used in this manner for fixing the mordant upon the fibre are termed *fixing agents*.

In some cases of mordanting, the cotton is first impregnated with the fixing agent (*e.g.* tannic acid, sulphated oil, &c.), then dried and afterwards passed through the mordant solution, as for example, in Turkey-red dyeing.

Special methods of mordanting cotton are occasionally adopted, in accordance with the properties of the metallic salt employed. Stannic oxide, for example, may be fixed on cotton by passing the fabric through a solution of sodium stannate, and then through dilute sulphuric acid, and finally washing Alumina is precipitated on the fibre by the mere exposure to air of cotton impregnated with sodium aluminate, in which case atmospheric carbonic acid is the active fixing agent.

The *chromium mordants* are of the first importance, since, with different colouring matters, they yield a considerable range of colours which are remarkable for their permanence. The most important chromium mordants are potassium and sodium dichromates, and they are more largely used as mordants in wool dyeing than all other metallic salts. In cotton dyeing they are not used as mordants, but are frequently employed as oxidising agents, *e.g.* to develop the colour in dyeing catechu brown or aniline black. Dichromates are also used in producing 'chrome yellow' and 'orange' (chromates of lead) on cotton. Chromium fluoride ($CrF_3,4H_2O$) is also used to a limited extent as a mordant for wool. Other chromium salts employed as mordants, chiefly for cotton, are chrome alum, chromium acetate, and various chromates of chromium. Chrome alum is obtained in large quantities as a by-product during the manufacture of alizarin; chromium acetate is prepared by mixing together solutions of chrome alum and lead acetate.

Wool is mordanted with chromium by boiling for 1–1½ hours in a solution containing 3 p.c. potassium (or sodium) dichromate calculated on the weight of wool. In many cases it is beneficial to add 1 p.c. sulphuric acid (sp.gr. 1·84) or 1·5 p.c. hydrochloric acid (sp.gr. 1·16), or 6 p.c. tartaric acid, or 1 to 2 p.c. formic acid, whereby fuller or brighter colours are ultimately obtained. ●When potassium dichromate alone is employed, partial decomposition of the salt occurs, accompanied by some reduction, the wool absorbing some chromic acid and chromium●chromate as well as potassium di-chromate. When an addition of●sulphuric acid is made, the wool ●bsorbs only chromic acid. In both cases the mordanted wool

has a yellow or buff colour, and only in the dye-bath does the reduction to the real mordanting body, chromic oxide, take place within the fibre through the interaction of the colouring matter. When formic or tartaric acid is the assistant employed, the mordanted wool has a green colour, reduction of the chromic acid taking place already in the mordanting bath, and chromic hydrate being deposited within the wool substance. If large amounts of potassium dichromate are employed in mordanting, especially if sulphuric acid is also added to the bath, bad results may be obtained through the colouring matter being oxidised and destroyed by the excess of chromic acid present in the wool. This defect is known as ' over-chroming.' In certain cases, potassium dichromate may be usefully applied in the same bath with the colouring matter (*e.g.* with alizarin), or by an after process (*e.g.* in the case of camwood).

Silk is not usually mordanted with chromium. It becomes mordanted, however, if boiled with a solution of potassium dichromate and tartaric acid after the manner of wool, but not if potassium dichromate alone, or with the addition of sulphuric acid, is employed. The fibre is somewhat injured by this process.

Cotton may be mordanted with chromium by impregnating it with a moderately concentrated solution of chrome alum, drying, and passing through a boiling solution of sodium carbonate or caustic soda. Better results are obtained by the use of ' chromium mordant G. A. I.' or ' G. A II.' (M. L. & B.), which are solutions of chromium chromates. Other satisfactory mordants for cotton are chromium bisulphite (Knecht) and sodium chromite (Koechlin). A method in vogue with the printer is to impregnate (pad) or print the cotton with a mixture of colouring matter and chromium acetate, dry and steam (' steam colours ').

The chief *aluminium mordants* employed for *wool* are aluminium sulphate and alum. The best results are usually obtained by boiling the wool for 1–1½ hours with a solution of 8–10 p.c. of the aluminium salt calculated on the weight of the wool, with the addition of cream of tartar, in the proportion of 3 mols to 1 mol. aluminium sulphate. Aluminium tartrate also gives excellent results, but it is cheaper to allow this salt to be formed in the mordanting bath itself in the manner described. With some colouring matters, oxalic acid or potassium binoxalate are to be preferred as assistants to cream of tartar.

Silk is mordanted by boiling with dilute aluminium sulphate solution, or by steeping 24 hours in a concentrated solution, and then washing in water, preferably calcareous.

The methods of mordanting *cotton* with aluminium are various. It may be impregnated with a moderately concentrated solution of alum or aluminium sulphate, dried, and then passed for a few minutes into a hot solution of sodium phosphate, arsenate, or silicate, or ammonium carbonate. Or the cotton may be impregnated with a cold solution of neutralised sulphated oil, or of tannic acid, then dried, and steeped in a solution of aluminium acetate or basic aluminium sulphate. Another method consists in impregnating the cotton with a solution of sodium alumihate, drying and exposing to the air, or passing through a solution of ammonium chloride. Normal and basic aluminium acetates are also employed, the cotton being impregnated with their solutions, then dried, and exposed to a moist warm atmosphere (' ageing '), and finally passed through a hot solution of, *e.g.*, sodium arsenate. The aluminium acetates employed are prepared by dissolving aluminium hydrate in acetic acid, or by decomposing a solution of aluminium sulphate with calcium or lead acetate (' red liquor '). The more basic the aluminium salts are, the more readily do their solutions precipitate by heating or on dilution with water, and the larger the quantity of alumina they yield to the fibre when used as mordants.

The chief *iron mordants* employed are ferrous sulphate and acetate, and ferric sulphate, acetate, and nitrate.

The ferrous acetate employed is made by dissolving scrap iron in pyroligneous acid. The ' pyrolignite of iron ' or ' black iron liquor ' thus obtained is preferable to that ,made by the mutual decomposition of ferrous sulphate and lead acetate solutions, being less liable to oxidise because of the presence of tarry matter and reducing agents, *e.g.* pyrocatechol, &c. Ferric sulphate is prepared by heating a mixture of definite proportions of ferrous sulphate, sulphuric acid, and nitric acid. Although the last-mentioned substance is only used as an oxidising agent, the final preparation is generally termed by dyers ' nitrate of iron.' The so-called ' pure nitrate of iron ' (ferric nitrate) is prepared by dissolving scrap iron in nitric acid.

Wool may be mordanted by boiling in a solution of 7 p.c. ferric sulphate $[Fe_2(SO_4)_3]$ and 4 p.c. potassium binoxalate, calculated on the weight of the wool, but iron is now very little used as a mordant for wool.

Silk may be mordanted by steeping for about 12 hours in a cold solution of pyrolignite of iron (sp.gr. 1·025), and afterwards washing well. The most usual mordant, employed largely in black-silk dyeing, is the basic ferric sulphate $Fe_4(SO_4)_5(OH)_2$. The silk is steeped in a somewhat concentrated solution of this salt (sp. gr. 1·25) for about 1 hour, then squeezed and well washed. The operations are repeated seven or eight times, after which the silk is boiled in an old soap-bath and finally washed. In this process, the very sensitive basic ferric sulphate absorbed by the fibre is decomposed during the several washings, a still more basic and insoluble salt being precipitated within the fibre.

Cotton is usually mordanted with iron by first impregnating it with a cold solution of tannin matter (*e.g.* myrobolans), and then, with or without drying, passing into a dilute solution of ferrous acetate, ferric sulphate, or nitrate (sp.gr. 1·01–1·02). The cotton may alternatively be impregnated with ferrous or ferric acetate, dried, and exposed to a moist warm atmosphere (' ageing '), finally fixing the mordant by passing through a hot solution of, *e.g.*, sodium phosphate.

Tin mordants are now rarely used, but if required the stannous salts are employed for *wool* and the stannic salts for *cotton*. The chief stannous mordant is stannous chloride or ' tin crystals.' It is frequently sold as a somewhat acid solution under the names of ' single muriate of tin ' (sp.gr. 1·3), or ' double muriate of

tin ' (sp.gr. 1·6). The general name ' tin spirits ' is given to a variety of solutions of tin in mixtures of hydrochloric, sulphuric and nitric acids.

Wool is mordanted by boiling in a solution containing 6 p.c. of the weight of wool of stannous chloride, and 6–10 p.c. cream of tartar. Large proportions of stannous chloride should be strictly avoided, otherwise the dyed wool feels harsh and its general properties are impaired.

Silk may be mordanted in the same manner as wool, or steeped several hours in a more or less concentrated solution of stannic chloride, and then well washed.

Cotton is mordanted with stannic oxide by impregnating the cotton with cold tannin solution (*e.g.* sumach) for 3 hours, then squeezing, and, with or usually without drying, steeping 1 hour in a dilute solution of stannic chloride (sp.gr. 1·02), and washing. Cotton thus mordanted was much used formerly for fixing mordant dyes—peachwood, logwood, &c , in which case the stannic oxide constituted the mordant, the tannic acid acting as fixing agent. Now that the basic coal-tar dyes are so much employed in dyeing cotton, although the same method of mordanting is employed, the *rôles* of the tin salt and tannic acid are reversed, for it is really the tannic acid which is the essential mordant, while the stannic chloride serves only as the fixing agent.

Acid mordants are employed for fixing basic colouring matters on cotton. They are not used in wool or silk dyeing, since these fibres themselves act as acid mordants, and are dyed directly without the aid of any external mordant

Tannic acid is the mordant *par excellence* for fixing the basic coal-tar colours on cotton This fibre absorbs tannic acid from its cold solution, and, when thus prepared, if immersed in a solution of a basic colouring matter, the tannic acid combines with the colour base, a coloured lake is formed within the substance of the fibre, and the cotton becomes dyed. During the dyeing process, the acid originally in combination with the colour base is displaced, and since in the free state it interferes with the complete formation of the colour lake, it is found beneficial to add a small proportion of sodium carbonate or acetate to the dye-bath. Since the tannates of colour bases are somewhat soluble, in excess of tannic acid or in alkaline (or soap) solutions, it is necessary in practice to fix the tannic acid on the fibre, previous to dyeing, in the form of an insoluble metallic tannate. This is done by passing the tannic-acid-prepared cotton through a hot or cold solution of tartar emetic or stannic chloride ; tannate of antimony or tin is thus fixed on the fibre, and these salts have as great an affinity for the colour base as free tannic acid has. Cotton thus mordanted and dyed is probably permeated with a very insoluble double tannate of antimony or tin and colour base ; a triple compound which is insoluble in alkaline solutions, and therefore fast to washing with soap, &c.

The tannin mordants, chiefly used by the dyer, are gall nuts and sumach, for light colours ; and myrobolans, divi-divi, quebracho, and chestnut extract, for dark colours and blacks.

As already pointed out, tannic acid is sometimes used as a *fixing agent* for tin, iron, or aluminium mordants, and since its iron compound is of a bluish-black colour, it sometimes serves as a useful *colouring matter.*

Tannic acid. is not used as a mordant·for wool, but for *silk* it is largely employed, partly for adding weight to the silk, and partly for the purpose of dyeing it black in conjunction with iron mordants. Its utility as a weighting agent is owing to the fact that under suitable conditions silk absorbs as much as 25 p.c. of its own weight of tannic acid from a hot solution, whereby the fibre gains not only in weight, but also in volume.

Fatty acids are used as mordants, very much in the same way as tannic acid, for fixing the basic coal-tar colours on cotton. They are, however, not attracted by cotton from their solutions, but they form insoluble lakes with the colour bases. The method of procedure is to impregnate the cotton with a more or less concentrated solution of their alkali salts, viz. soap ; after drying, the fabric is passed through, or preferably steeped in, a cold solution of aluminium sulphate, and washed. Although the fatty acid is thus fixed on the fibre as an insoluble aluminium soap, it is still capable of combining with the colour base when the cotton is passed into a solution of a basic colouring matter Colours dyed by this method are brighter than, but not so fast to washing as those fixed by means of tannic acid

Instead of ordinary soap, a more convenient fatty-acid mordant to employ is the so-called ' sulphated oil.' This is prepared by mixing two parts by weight of castor oil with about one part of sulphuric acid (sp.gr. 1·84), and allowing the mixture to stand for 24 hours. It is then washed with a strong solution of common salt to free it from excess of acid, and is finally neutralised with ammonia or caustic soda. The product of the action of the acid upon the oil is somewhat complex, but its practical utility depends upon the fact that it behaves like a fatty acid and gives an extremely soluble soap with alkalis. Ordinary castor-oil soap produced by boiling the oil with caustic soda is also very soluble, and may be used as a mordant. Sulphated oil is frequently called ' Turkey-red oil,' ' alizarin oil,' and ' soluble oil,' since it is largely used in the modern short process of Turkey-red dyeing as the fixing agent for the necessary aluminium mordant, and it gives the characteristic brilliancy of colour obtained by the use of the oil preparations formerly employed. Monopole oil is a similar product.

Phenolic colouring principles, *e.g.* alizarin, and certain acid colouring matters derived from benzidene, stilbene, fluorene, &c. (the direct cotton dyes) can also be fixed on cotton, and serve as mordants for basic colouring matters, but they are only occasionally used for this purpose for the production of compound shades.

COLOURING MATTERS.

(For Classification, see p. 575).

GENERAL METHODS OF APPLICATION.

CLASS I.—**Mordant dyes.** This group of dyestuffs includes the majority of the *natural dyes,* also the numerous class of *alizarin dyes,* a number of derivatives of *pyrogallol* and other *phenols,* and certain *azoquinone-oximes* and *nitroso- dyes.* The following are the chief members of the group.

Mordant dyes of natural origin—Logwood; madder; cochineal; limawood and other 'soluble redwoods'; camwood and other 'insoluble redwoods'; fustic; weld; quercitron bark and flavin.

Synthetic mordant dyes.—Alizarin; anthrapurpurin, flavopurpurin, and purpurin; nitroalizarin (alizarin orange); alizarin maroon (aminoalizarin); alizarin bordeaux; anthracene brown; alizarin blues; alizarin cyanins; anthracene blues; alizarin greens; cœrulein; anthracene yellow; mordant yellow, galloflavin, &c.; alizarin black; gallein; gallocyanin; cœlestine blue; naphthol green, dark green, gambine, &c.

The mordant dyes are largely used in the dyeing of wool and in the dyeing and printing of cotton and silk. Generally speaking, they yield colours which are of great fastness to light, soaping, acids, alkalis, bleaching agents, &c As regards cotton dyeing, they have largely been replaced by 'after-treated' direct dyes and the very fast vat and sulphide dyes recently introduced.

When a fabric, previously mordanted with a metallic salt, is dyed with a mordant dye, a chemical reaction takes place, resulting in the formation of a new compound which is the actual colouring substance; this compound being, at the same time, fixed upon the fibre, which thus becomes dyed. These *colour lakes* or *pigments* may, for the most part, be equally well produced by bringing together the mordant and the dyestuff under suitable conditions in the absence of the fibre. Many colour lakes of this class are indeed manufactured in bulk for use in printing or painting.

There are three methods by which mordant dyes may be applied : (1) the mordant may be first applied to the fibre, and afterwards the dyestuff in a separate operation (' mordanting and dyeing method '); (2) the order of application of mordant and dye may be reversed (' dyeing and saddening method '); or (3) the mordant and dyestuff may be applied simultaneously (' single-bath method '). All three methods are in use. If equally good results can be obtained, the ' single-bath ' process is to be preferred, but usually the ' mordanting and dyeing ' process gives the maximum fastness.

The dyeing of wool with mordant dyes.— When potassium dichromate is employed as mordant, the ' *mordanting and dyeing* ' process is usually preferable, because, in the ' single-bath ' process, the acid necessarily added to dissolve the colour lake formed in the dye-bath, converts the mordant into such a powerful oxidising agent by liberating chromic acid, that most dyestuffs are injuriously affected. In the two-bath process, the wool should be thoroughly washed after mordanting. If this operation is omitted, a portion of the mordant passes from the wool into the dye-bath, and, combining with an equivalent amount of colouring matter, forms a precipitate which floats about in an insoluble condition. This not only leads to loss of dyestuff, but also tends, by superficial absorption, to cause the dye to 'rub off.' The dyeing process consists in boiling the wool for from 1 to 2 hours with the colouring matter in aqueous solution. The final washing, after dyeing, has for its object the removal of any colouring

matter which is imperfectly fixed ; but, however thorough the washing may be, there is usually a small amount of colouring matter present on the dyed wool, which has merely been absorbed without combining with the mordant. This free colouring matter will dissolve out or ' bleed ' during milling or scouring, because most mordant dyes are readily soluble in alkaline solutions. A slight supplementary mordanting (' afterchroming ') is frequently used to fix this small amount of free dyestuff.

The ' *dyeing and saddening* ' method is not much used with the true mordant dyestuffs, but is the chief process used in applying the *acid mordant dyes*. Since the ultimate intensity of colour depends chiefly upon the amount of dyestuff which is fixed in the first bath, whilst the colour is only developed by the mordant in the second bath, it is obviously more difficult to exactly match a pattern when this process is used than when the mordant is applied first.

In the ' *single-bath* ' method ,of dyeing, the bath is prepared with the necessary amount of mordant and dyestuff with an addition of sufficient acid (usually oxalic or acetic acid) to dissolve the colour lake formed. This process is therefore only suitable when the colour lake is soluble in dilute acid, and thus is particularly characteristic of the tin and aluminium colour lakes : although the single-bath process is also frequently applicable in the case of ferrous sulphate or chromium fluoride mordants.

The dyeing of silk with mordant dyes.—The mordant dyes are not very largely used on silk, chiefly because they detract somewhat from the lustre of the fibre. The degree of fastness of the acid dyes, if suitably selected, is, moreover, usually sufficient for the requirements of the silk dyer. The methods of mordanting have already been dealt with. Dyeing must take place at the boil for about an hour, and the silk is subsequently brightened by working in a warm dilute solution of acetic or tartaric acid, and dried without washing.

Dyeing of cotton with mordant dyes.—The ' mordanting and dyeing ' method is generally used in cotton dyeing Aluminium is the chief mordant employed, and, in conjunction with alizarin, it yields the important Turkey-red dye. This is a complex compound containing an alizarin-aluminium-calcium lake in combination with polymerised fat acids. In the production of this colour, the cotton is first prepared with sulphated oil, then dried, mordanted with alum, and subsequently dyed with alizarin. The complete process involves a large number of operations, for the details of which manuals of dyeing must be consulted. The dyeing of Turkey red is a very ancient process, having been carried out centuries ago in India by the aid of milk (as fatty matter) and munjeet, the Indian madder plant. No alum was employed, but the plant with its earthy incrustations contained sufficient alumina to produce the alumina lake. The art spread from the East through Persia and Turkey, and was first introduced into this country (Glasgow) in 1790. Madder has now been entirely replaced by synthetic alizarin in Turkey-red dyeing, and the substitution of ' sulphated oil ' for olive oil or soap has also greatly simplified the process.

Another important mordant dye on cotton

is logwood black, which is obtained by dyeing with logwood on tannin-iron mordant. It is largely used in hank and warp dyeing. Catechu brown is produced by the 'dyeing and saddening' method, the cotton being first steeped in a strong solution of catechu, and subsequently treated with potassium dichromate. The latter acts essentially as an oxidising agent, producing the so-called *japonic acid* on the fibre.

A great variety, of permanent and bright colours may be obtained with mordant dyes on cotton mordanted with chromium or aluminium, but they are not very largely used, fast colours being chiefly produced by means of the *sulphide, vat,* and *ingrain* dyes (Classes VI., VII, VIII).

CLASS II.—Acid-mordant dyes. These dyes are suitable only for wool and silk, and are largely used on wool. They are now very numerous, and are chiefly azo- compounds containing salicylic acid or orthoaminophenol components. Some, however, are anthracene or pyrogallol derivatives. Unlike the mordant dyes, they usually contain sulphonic acid groups.

Many of the acid-mordant dyes may be employed as ordinary acid dyes, since a mordant is not essential to the development of their colour. Usually, however, such dyestuffs produce faster colours when applied in conjunction with a mordant.

An exhaustive list of acid-mordant dyestuffs cannot be given, but the following will serve as examples. They include dyes giving a complete range of colours. *Reds* : acid-alizarin, anthracene, chrome, cloth and milling reds. *Oranges and yellows* : cloth oranges and yellows, alizarin yellows (certain marks are mordant dyes), chrome yellows, milling orange and yellow, diamond, and mordant yellow. *Greens* : acid-alizarin, chrome, diamond and milling greens. *Blues* : acid-alizarin, brilliant-alizarin and chrome blues ; chromotropes (chromotropes dye red as acid dyes). *Violets* : alizarin heliotropes ; anthraquinone and chrome violets ; fast violet. *Blacks and greys* : acid-alizarin, acid-chrome, anthracene-acid, anthracene chrome, chrome, chromotrope and diamond blacks. *Browns* : acid-alizarin, acid-anthracene, chrome, cloth, diamond, and palatine browns ; chromogen.

Dyeing of wool with acid-mordant dyestuffs.— The usual method of application of this class of dyestuffs is to prepare a bath containing the necessary amount of dyestuff along with 1 to 3 p.c. sulphuric or 3 to 5 p.c. acetic acid, and 5 to 10 p.c. sodium sulphate (Glauber's salt) (all calculated on the weight of wool). After the solution has been brought gradually to the boiling-point, the boiling is continued until the colouring matter is entirely fixed, an additional amount of acid being added if necessary. Excess of acid, however, frequently retains the dyestuff in solution. The wool is then removed from the bath, the metallic salt is added, and the wool is again boiled in the bath for half an hour. In most cases, potassium dichromate, to the extent of one-half the weight of the dyestuff, is the mordant employed.

A modification of this process is used with the *metachrome* series of dyestuffs. The *metachrome mordant* is a mixture of yellow potassium chromate and ammonium sulphate. The bath is prepared with 3 to 5 p.c. of this mordant

together with the dyestuff. A prolonged boiling is necessary, during which the ammonium salt is decomposed, ammonia being evolved and the liberated sulphuric acid gradually converts the chromate into dichromate and assists in the fixation of the dye and the formation of the colour lake.

The *anthracene chromate dyes* are applied in a bath containing colouring matter, dichromate, and sodium sulphate ; this being another modification of the usual process.

The mercerol and autochrome dyes are also applied by special processes.

The acid-mordant dyes are of increasing importance in wool dyeing, but are little used on silk, and not at all on cotton.

CLASS III.—Acid dyestuffs. The acid dyes constitute the most numerous class of synthetic colouring matters. The chief chemical groups of acid dyes are *azo- dyes, nitro- compounds, sulphonated basic dyes,* and *phthaleins* ; the greatest number being azo- dyes. The azo- dyes contain few greens, blues, and violets ; but the reds, oranges, yellows, browns, and blacks are very numerous. The nitro- compounds are few in number and are all yellows, the chief being picric acid and naphthol yellow. The greater number of the sulphonated basic dyes, on the other hand, are greens, blues, and violets, but acid magenta belongs to this group. The resorcin or phthalein dyes are chiefly brilliant pinks or reds, the eosins being the most important group.

So extremely numerous are the acid dyes, and their names are so varied, that no useful purpose would be served by the enumeration of a small number of the products.

The dyeing of wool with acid dyes.—The commercial acid dyes are, in most cases, the sodium salts of sulphonic acids. The nitro- compounds, however, owe their acid character to the presence of nitro- groups in the molecule.

The simplest and most usual method of dyeing acid colours on wool is to prepare a bath containing the requisite amount of dyestuff with 1 to 4 p.c. of sulphuric acid and 10 to 20 p.c. of sodium sulphate (Glauber's salt). The wool is dyed in this solution for about an hour, boiling for the greater part of the time. Some dyes require smaller, and some larger percentages of acid. The sodium sulphate has a levelling influence on the fixation of the dyestuff, probably by reason of the solvent action which it exerts, since acid dyes are readily removed ('stripped ') from wool by boiling in a solution of sodium sulphate. Another reason is to be found in the retarding action which it exerts in the liberation of the free colour acid by the sulphuric acid. The equation, which may be expressed as :

$$\text{Colour salt} + H_2SO_4 \rightleftarrows \text{colour acid} + Na_2SO_4,$$
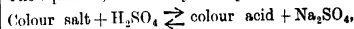
is reversible. (See also M. Firt, Theory of the Acid Dyebath, J. Soc. Dyers, 1916, p. 33.)

Sodium bisulphate or 'nitre cake' may be used in place of the sulphuric acid and sodium sulphate, or the sulphuric acid may be entirely replaced by acetic or formic acid.

In the case of dyestuffs which do not readily produce level colours on the fabric, the acid may be added to the bath gradually in small portions at a time, or may be substituted by an ammonium salt, e.g. ammonium sulphate

or acetate. The acid is then liberated very gradually as the ammonium salt is decomposed in the boiling bath, and the colouring matter is therefore converted very slowly from the condition of the soluble sodium salt to that of the more or less insoluble free sulphonic acid.

The dyeing of silk with acid dyes.—Acid dyes are very largely used in silk dyeing. They are applied in a bath containing a large quantity (up to 25 p.c. in volume) of 'boiled-off' liquor, the soapy solution of the silk gum obtained in the 'ungumming' of raw silk. The bath is rendered slightly acid by means of sulphuric, acetic, or formic acid. Dyeing usually takes place at about 80°, at which temperature silk has more affinity for acid dyes than in a boiling bath.

After dyeing, the silk is washed and is then 'brightened' by working in a dilute (sulphuric, acetic, or tartaric) acid solution and dried without washing.

The dyeing of cotton with acid dyes.—There is no satisfactory method of fixing the acid dyes upon vegetable fibres, but for cheap work they are often applied by a 'padding' process.

CLASS IV.—**The direct dyes.** The direct dyes have the special property of dyeing cotton without the aid of a mordant. Like the acid dyes, they are for the most part azo- compounds, but contain the chromophor $-N=N-$ twice in the molecule, and thus belong to the tetrazo-group of azo- dyes. They further resemble the acid dyes in that they are alkali salts of sulphonic acids, but as regards dyeing properties, they differ greatly from the simpler azo-acid dyes. Since the introduction, in 1884, of the first of the direct dyes, a very large number have been placed on the market, and the group contains dyes of all colours—reds, oranges, yellows, greens, blues, violets, browns, and blacks. As examples of these dyes may be mentioned the congo, benzo, diamine, mikado, titan, and chlorazol dyes.

Primuline is an example of a direct dye which is not an azo- compound. It contains the chromophor $\genfrac{<}{}{0pt}{}{S}{N}\geq C-$.

Turmeric is the only important natural direct dye for cotton.

The direct dyes are largely used upon all fibres. No satisfactory explanation has been given of the fact that they readily dye cotton, whereas the acid dyes are entirely devoid of this property. The further fact that the direct dyes dye wool in a neutral, or even slightly alkaline bath, whereas the acid dyes require the addition of acid, also requires explanation.

The dyeing of wool with direct dyes—These colouring matters are applied to wool in a neutral or feebly acid bath with or without the addition of sodium sulphate (Glauber's salt). In some cases, an after-treatment with a metallic salt gives improved fastness, the dyes then practically falling into the class of acid-mordant dyes.

As a class, the direct dyes on wool are much faster to milling than the ordinary acid dyes. When fixed on wool, they are also faster to acids, washing, and light than when dyed on cotton. In some cases, the colour produced by a direct dye on wool and cotton is identical, in other cases it differs considerably.

The dyeing of silk with direct dyes.—These dyes are largely used on silk both for self shades

and also on account of their property of permanent reduction to colourless bodies, in the so-called 'foulard' style of printing. They are applied in a similar manner to the acid dyes, but smaller amounts of 'boiled-off liquor' and acid are required.

The dyeing of cotton with direct dyes.—The application of the direct dyes to cotton is very simple. They are dyed either from a cold, luke-warm, or boiling solution, to which is added a small amount (up to 2 p.c.) of sodium carbonate, and an amount of a neutral salt (up to 20 grams $NaCl$ or Na_2SO_4 per litre), which is governed by the solubility of the dyestuff employed. At low temperatures more concentrated solutions of colouring matter are required. Brighter colours are obtained by passing the dyed material through a solution of Turkey-red oil before drying or by adding this substance to the dye-bath.

Mercerised cotton has a much greater affinity than ordinary cotton for the direct dyes, and in dyeing this fibre special precautions are necessary to produce level colours.

Many of the direct dyes produce on cotton colours of great brilliance and richness, but they bleed out into hot water, and are still more readily attacked by soap. Most of them are also comparatively fugitive to light.

There are three processes by means of which the fastness-properties of certain of the direct dyes can be improved.

1. *The diazotising and developing process.*—This process is applicable only in the case of those dyestuffs in which amino- groups constitute the auxochrome. The cotton is first dyed by the general process above described, then washed, and afterwards worked for a few moments in a cold dilute solution of nitrous acid (2 p.c. $NaNO_2$ and 4 p.c. HCl on the weight of the cotton). This treatment diazotises the amino- groups The cotton is then well washed in cold water and entered immediately into the developing bath, which contains a solution of a phenolic or amino- compound; sufficient alkali or acid respectively being added to bring the 'developer' into solution. The chief developers used are phenol, resorcinol, α- or β-naphthol, aminonaphthol, aminodiphenylamine, m-tolylenediamine, and certain of the naphthol sulphonic acids.

Primuline is applied by the process just described.

A modification of this method is known as the '*coupling process.*' The cotton is first dyed with the direct dye, and, after rinsing, is worked in a diazotised solution of the 'coupler.' The chief body used as coupler is p-nitraniline. Ready prepared stable diazo- compounds of this base are sold under the names 'nitrazol,' 'azophor red,' and 'nitrosamine red.'.

2. *After-treatment with metallic salts.*—In this process for improving the fastness of the direct dyes on cotton, the fibre is first dyed in the ordinary way, and then, after rinsing, is treated for half an hour in a warm slightly acidified solution of a suitable metallic salt. The salts chiefly employed are copper sulphate, potassium dichromate, and chromium fluoride; from 1 to 3 p.c. with addition of 2 to 4 p.c. of acetic acid being used. A mixture of the two first-mentioned salts is frequently used. This process is mainly employed in the case of blues, greens,

browns, and blacks. The chromium salts exert the greatest influence in increasing the fastness to washing, and the copper salt in regard to the fastness to light.

This process is only applicable to the case of dyestuffs containing free OH or COOH groups.

3. *After-treatment with formaldehyde.*—This process, which is chiefly used for navy blues and blacks, is carried out by working the dyed cotton for half an hour at 70° in a solution containing about 3 p.c. formaldehyde (on the weight of the cotton). The fastness against washing is considerably improved thereby.

Cotton dyed with direct dyes may be 'topped' with basic dyes, for which the direct dyes act as mordants.

CLASS V.—**The basic dyes.** This group of colouring matters is numerically smaller than the mordant, acid, or direct dye groups. It includes, however, the most brilliant dyes known, rhodamine pink, auramine yellow, malachite green, methylene blue, and methyl violet being well-known examples.

The basic dyes are very diverse in their chemical constitution Many are derivatives of di- or tri-phenylmethane (magenta, malachite green, methyl violet); others are azo- compounds (chrysoidine, Bismarck brown); some are azine-derivatives (safranine and induline); whilst the thiazines contain sulphur as an essential constituent (methylene blue).

The commercial basic dyes are usually hydrochlorides of the colour bases, but some are acetates, oxalates, sulphates, or zinc chloride double salts. They are characterised by great tinctorial power, 1 p.c being usually sufficient to produce a full rich colour. As a class, they are not fast to light.

Janus dyes. These occupy an intermediate position between the basic and the direct dyes. They are azo- dyes of strongly basic character, and possess an extraordinary affinity for both animal and vegetable fibres. They are only of slight importance.

The dyeing of wool with basic dyes.—These dyes are little used on wool, the acid dyes being applied in an equally simple manner and producing faster colours. Wool has a strong affinity for basic dyes, and readily becomes dyed if immersed in their solutions. A small amount of sulphuric or acetic acid may usually be added with advantage. Certain of the basic dyes, *e.g.* Victoria blue, are very fast to milling when dyed on wool, and such are still employed.

The dyeing of silk with basic dyes.—Members of this group of colouring matters are largely used by the silk dyer when fastness to light is not important. The silk yarn is dyed at 60°-80° in a slightly acidified solution of the dyestuff, to which is added some 'boiled-off liquor.' After rinsing, the dyed silk is brightened in a dilute solution of acetic or tartaric acid.

The dyeing of cotton with basic dyes.—Cotton has little affinity for basic dyes, which, on this fibre, must therefore be applied in conjunction with a mordant, and since the dyestuffs of this class are basic in character, the mordant must be of an acidic nature.

Three types of acid mordants are available, viz. : tannin matters, fat acids, and colour acids.

1. *Tannin mordants.*—As mentioned in dealing with the mordants, cotton has a natural affinity for tannic acid, which it withdraws from solution. Since tannic acid forms lakes with the basic colouring matters, cotton thus prepared may be dyed with basic dyes, but the colours produced in this manner are not fast against washing. As previously explained, however, if after mordanting with tannin the cotton is treated with a salt of antimony, tin, or iron, an insoluble metallic tannate is formed on the fibre, which compound has the same affinity for basic dyes as tannic acid has. The fastness properties of the double tannate of colour base and metal are much superior to those of the simpler tannates of the colour bases.

For the production of pale or bright colours, commercial tannic acid, gall nuts, or sumac are the tannins employed. The cotton is saturated ('padded') with a solution of 2° to 3°Tw. strength, or steeped for 2 to 3 hours in a solution containing 2 to 5 p.c tannic acid or 10 to 30 p.c. ground gall nuts or sumac; the amount being calculated on the weight of cotton. The yarn or fabric after squeezing is then at once passed into a 'fixing bath' containing 1 to 2·5 p.c. of tartar emetic or an equivalent amount of antimony oxalate or fluoride After well washing, the cotton is dyed with 0·1 to 1 p.c. of basic dye.

Additions of acetic acid to the tannin bath, ammonium chloride and chalk to the fixing bath, and a little acid to the dye-bath, are frequently made. The mordanting and fixing baths may be used for several successive lots of material.

If the brightest possible shades are not required, some cheaper tannin matter (myrobolans or quebracho) may be employed, and stannic chloride may replace tartar emetic as fixing agent. For dark shades, ferrous acetate ('black iron liquor') is used as fixing agent, the blueblack tannate of iron producing a composite colour with the basic dyestuff.

2. *Fatty mordants.*—If Turkey-red oil or soap is used as mordant, the colour produced with a given basic colour is brighter, but less fast, than when tannin mordant is used.

The fat acids are fixed on the cotton as metallic salts, usually aluminium salts; the fibre being first saturated with a solution containing 1 lb. of sulphated oil or soap per litre, then dried and passed into a solution of aluminium acetate ('red liquor') of about 8°Tw.

3. *Colour acids as mordants.*—Mention has already been made of the fact that the direct dyes act as mordants towards the basic dyes, compound shades being thus obtained. Mordant, sulphide, and acid dyes also possess the property of attracting basic dyes, but these combinations are not much employed.

The dyeing of jute with basic dyes.—Although jute is a vegetable fibre, it does not consist of free cellulose, but of a bastose-cellulose compound, *corchorobastose* (Cross and Bevan). The dyeing properties of this substance differ materially from those of cellulose; jute, in fact, behaving in a very similar manner to tannin-mordanted cotton, and dyeing direct with basic dyes.

CLASS VI.—**The sulphide dyes.** The dyes of this group are numerous and important. They are chiefly employed for the production of fast blacks, blues, greens, browns, and yellows on cotton and other vegetable fibres. They come into the market in the form of powders, which

are usually insoluble in water, but soluble in solutions of sodium sulphide. They are also rendered soluble by other reducing agents, *e.g.* sodium hydrosulphite or glucose in alkaline solution.

The sulphide dyes are commercially known under such names as : sulphur, sulphurol, thiogene, thionol, thional, thioxine, cross-dye immedial, katigen, kryogen, pyrogen, pyrol rexoll, eclipse, vidal, or auronal dyes. They are produced by melting together under suitable conditions aromatic nitro-, amino-, or imino-compounds with sulphur and sodium sulphide. The constitution of the sulphide dyes is not known, but the commercial products are probably mixtures of polymers or homologues and not homogeneous bodies. They contain free sulphur in amount varying from 1 to as much as 12 p.c. (Gardner and Hodgson, J. Soc. Chem. Ind. 1910, 672), and also contain very variable amounts of sodium sulphide and polysulphides.

The dyeing of wool with sulphide dyes.—Wool is rarely dyed with sulphide dyes, on account of the injurious action of sodium sulphide on the fibre. The wool may be protected to some extent against this action by the addition to the dye-bath of glucose, tannic acid, or ammonium salts. A previous treatment of the fibre with formaldehyde has also been recommended (R. Kann, Eng. Pat. 3492, 1903), but this reduces the affinity of the wool for these dyestuffs.

Greater success in the application of sulphide dyes to wool or union material has been attained by E. Lodge (Eng. Pats. 19852, 1913 ; and 23386, 1914) by the use of sodium hydrosulphite and sodium sulphite as reducing agents, and ammonia as solvent for the reduced dyestuff (J. Soc. Dyers, 1915, 252).

The dyeing of silk with sulphide dyes.—Owing to the harmful effect of their alkaline solutions upon the silk fibre, the sulphide dyes are not used.

The dyeing of cotton with sulphide dyes.— This group of dyestuffs is now of the greatest importance in cotton dyeing for the production of fast blacks, and to a less extent, fast blues, greens, browns, &c. The necessary ingredients in the dye-bath, in addition to the dyestuff, are sodium sulphide, sodium sulphate, or other neutral salt, and an alkali, usually sodium carbonate. The actual and relative amounts of these substances vary considerably with different dyestuffs, depending upon the ease with which the colouring matter employed undergoes reduction and the solubility of the reduced product. An addition of Turkey-red oil, monopole oil, or glue, tends to produce more level and brighter shades ; glucose aids the reduction. Dyeing takes place just below the boil, and it is usually desirable to keep the cotton completely immersed during the operation, in order to prevent irregular oxidation. The baths are used in a very concentrated condition, with the result that only a small proportion of the dyestuff is withdrawn, and for reasons of economy ' standing baths ' are employed, that is, the baths are used continuously and replenished with dyestuff, &c., as required. The dyeing takes place in iron, wooden, or lead-lined wooden vessels ; copper being rigidly excluded, on account of the ease with which it is attacked by sodium sulphide.

Some of the sulphide dyes do not require any treatment subsequent to dyeing other than

exposure to air, but with many dyes of the group an after-treatment greatly improves their fastness to light and other influences. The chief object of the after-treatment is to ensure the complete oxidation of the colouring matter ; and, as oxidising agents, chromium salts, or hydrogen peroxide are used. Steaming the material in presence of air is employed in the case of immedial blue.

After-treatment with potassium dichromate and acetic acid is now usually practised, since the use of copper salts has proved to be dangerous in regard to the subsequent tendering of the fibre on account of their catalytic action in inducing acid formation (Gardner and Hodgson, J. Soc. Chem. Ind. 1910, 676).

The tendering of cotton dyed with sulphide blacks has greatly retarded the use of these dyestuffs. The defect does not usually develop for some weeks or months after the material has been dyed, and it has been shown to be due to the slow formation of sulphuric acid on the fibre. The development of acid arises mainly from the oxidation of free sulphur present on the dyed fibre, but even in the absence of free sulphur, acid development may take place by decomposition and oxidation of the colour molecule.

The risk of tendering, during storage, of cotton dyed with sulphide blacks is entirely eliminated by a final treatment of the material, before drying, with sodium acetate ; but, of course, the protective influence of this salt disappears if the material is washed.

CLASS VII.—**The vat dyes.** Until comparatively recently, indigo was the sole representative of this group of dyestuffs. The synthetic production of indigo was, however, followed by that of a number of derivatives of this body. Other series of vat dyes have also been produced, and by their use it is now possible to produce on cotton, and in a .more limited degree on wool, many bright colours of a degree of fastness hitherto unattainable.

The essential features of a vat dye are its easy reduction to a form soluble in dilute alkali, its attraction in this condition by the fibre, and its ready reoxidation on the fibre to the original insoluble condition. The reduced solution is termed the ' vat,' the composition of the vats differing for wool and for cotton.

The vat dyes are mainly derivatives of indigotin or anthracene. They include the following : indigo (indigotin) ; mono-, di-, tri-, and tetra-halogen derivatives of indigotin ; methyl and tolyl indigotins ; ciba dyes (brom indigotins) ; thioindigo red and scarlet ; helindone dyes (sulphur derivatives) ; algole dyes ; cibanone dyes, and the indanthrene dyes. The group includes dyes of all hues.

Indigo is the oldest and by far the most important of the vat dyes. It has been employed in India for at least 3500 years, by methods not differing essentially from some of those which are still employed. It is used upon all fibres, but least commonly upon silk.

Various reducing agents are employed for the conversion of the insoluble indigo blue into indigo white, and they are always associated with an alkali to dissolve the latter substance. After saturating the fibre with the alkaline solution, the indigo white is reconverted into

indigo blue upon the fibre by atmospheric oxidation.

The dyeing of wool with indigo vat blue.—The two chief indigo vats used for wool are the fermentation vat and the hydrosulphite vat, the former being chiefly used for dark shades on woollen cloth (Army and Navy cloth, &c.), and the latter for light colours on slubbing, yarn, &c. There are several forms of fermentation vat, of which the woad vat is the most important in this country. The precise composition and 'setting' of the vat is largely a matter of experience, the ingredients being somewhat as follows : finely ground indigo, 12 to 18 lbs. ; woad, 300 lbs. ; bran, 10 lbs. ; madder, 12 to 18 lbs. ; lime, 12 lbs. ; water, 600 gallons. After warming the liquor, various fermentations set in, the essential bacterium being the *Desmobacterium hydrogeniferum*. The starchy matters present are first converted into glucose, which then splits up into lactic acid, the latter undergoing butyric fermentation with evolution of hydrogen.

Excessive fermentation is prevented by making suitable additions of lime, or it is accelerated, if necessary, by adding further quantities of bran.

In the so-called German or soda vat and the Indian or potash vat, the woad is replaced by bran with the addition of molasses, and the lime by sodium or potassium carbonate.

To avoid the derangements to which all fermentation vats are liable, Collin and Benoist (J. Soc. Chem. Ind. 1885, 493) proposed to employ a pure ferment and a completely fermentable food material ; but this process has not come into practical use.

Natural indigo is still largely used in the fermentation vats, but in the hydrosulphite vat the synthetic product is generally employed. The hydrosulphite vat may be prepared as follows : synthetic indigo (20 p.c. paste), 10 lbs. ; caustic soda solution 42°Tw., 3 pints ; sodium hydrosulphite solution 20°Tw., 7½ gallons; water, 50 gallons. The liquid is heated to 50° until it becomes clear greenish-yellow. The solution of indigo white thus obtained is diluted to 250 gallons with water at 50°, to which a little hydrosulphite has been previously added.

The hydrosulphite solution may be replaced by 3 lbs. of solid sodium hydrosulphite, in which case the amount of caustic soda must be increased. 3½ lbs. of natural indigo (60 p.c. indigotin) are about equivalent to 10 lbs. of synthetic indigo (20 p.c. paste). After working in the vat, the goods are well squeezed, and then exposed to the atmosphere to oxidise the indigo white : they are then well washed.

Dark shades of indigo blue on wool are usually 'bottomed,' with a red dye (alizarin, diamine fast red, or barwood) before vatting, and are frequently 'topped' after vatting with orchil or other dyestuff in order to add 'bloom' to the colour.

In most respects indigo vat blue is an extremely fast colour, but has the defect of being liable to 'rub off.'

The dyeing of silk with vat indigo.—This dye is not much employed on silk. If used, the most suitable vat to employ is the hydrosulphite vat set with synthetic indigo.

The dyeing of cotton with vat indigo.—The

hydrosulphite vat is largely employed in cotton dyeing as well as in the dyeing of wool, but it is used cold in the case of cotton. Other cotton vats are the 'copperas vat' and the 'zinc-powder' vat.

A strong copperas vat contains, indigo (60 p.c.), 10 lbs. ; ferrous sulphate, 30 lbs. ; and quicklime 35 lbs., in about 200 gallons of water. The lime decomposes the ferrous sulphate, with the production of ferrous hydroxide, and this in the presence of lime and indigo decomposes water, yielding ferric hydroxide and hydrogen ; the latter at once combines with the indigotin and produces indigo white, which dissolves by reason of the excess of lime present. The normal colour of the vat liquor thus obtained is brownish-amber.

The zinc-powder vat is made up with water, indigo, zinc-powder, and lime. In the presence of the lime and indigo, the zinc decomposes water even at the ordinary temperature, and the liberated hydrogen effects the reduction of the indigo.

Vat dyes other than indigo.—These may be divided into two groups : (a) the *indigoids*, which may be considered as derivatives of indigotin ; and (b) the *anthracene* derivatives. They all possess the common property of forming vats when treated with hydrosulphite of soda, but whereas the indigoids may be applied to the animal as well as to the vegetable fibres, the anthracene derivatives are only suitable for cotton on account of the large amount of caustic alkali required for their solution. The reduced anthracene vat dyes also do not appear to possess much affinity for wool.

(a) *Indigoids.*—Examples of dyes of this series are : thioindigo red and scarlet ; helindone red and scarlet ; ciba red and scarlet ; vat red ; helindone orange and yellow ; ciba green ; brom indigos ; ciba blues and greys; ciba violets and helidtropes ; helindone brown. Some of the algole reds also probably belong to this group.

(b) *Anthracene vat dyes.*—Indanthrene red ; algole reds ; indanthrene yellows and oranges ; algole yellows and oranges ; cibanone yellows and oranges ; indanthrene greens ; algole greens ; indanthrene, chloranthrene, duranthrene and caledon blues ; algole blues ; indanthrene grey ; indanthrene browns ; algole browns ; cibanone browns.

The application of the indigoid vat dyes to wool and silk—Vats suitable for the dyeing of wool and silk are obtained by reduction with sodium hydrosulphite in alkaline (caustic soda) solution. Bright reds of excellent fastness are obtained with these dyes, and they are used in conjunction with indigo for producing bright purplish blues. Separate vats are preferable for the indigo blue and the red dye, since the best conditions of dyeing do not coincide in the two cases.

The application of indigoid vat dyes to cotton. —Vegetable fibres are readily dyed with these dyes from a hydrosulphite vat, or alternatively they may be dyed from a sodium sulphide bath, as used for the sulphide dyestuffs. They may be mixed with most sulphide dyes and dyed from the same vat.

The application of the anthracene vat dyes.— This group of dyes is also applied in the hydrosulphite vat, but usually requires such a strongly

caustic solution that its application to wool and silk is not practicable.

By use of the vat dyes, it is now possible to produce a great variety of colours on cotton which are extremely fast to light, washing, bleaching, and other influences. The high cost of these dyes at present somewhat limits their application.

Indophenol is a vat dye of different type, being obtained by the action of nitroso-dimethyl aniline on a-naphthol. On reduction, it is converted into *indophenol white*, a body sufficiently stable to admit commercially. On oxidation with chromic acid, indophenol white is reconverted into indophenol blue.

Indophenol has been employed in conjunction with, or as a substitute for indigo, but has the defect of being readily affected by acids.

Tyrian purple.—As the result of an extremely interesting investigation, P. Friedländer has shown (Ber. 1909, 765) that this ancient dyestuff is identical with one of the dibrom-indigotins. Tyrian purple, as described by Pliny, was obtained from various species of the mollusc *murex*, and from 12,000 of the species *M. brandaris* Friedländer obtained 1·4 grams of the colouring matter.

Under the law of the ancient Romans, the use of Tyrian purple was confined to royalty, and the method of its production was a lost art for many centuries. At the beginning of the 18th century, it was investigated by Reaumur (Mem. de l'Acad. Royale des Sciences, 1711), but it never again assumed any importance as a dye-stuff.

CLASS VIII.—**The ingrain dyes.** The term *ingrain dye* may be used to designate those colouring matters other than mordant dyes which are produced from their constituent bodies *upon the fibre*. Three sub-groups may be distinguished : (*a*) *aniline black* ; (*b*) *the insoluble azo- dyes* ; and (*c*) *the metallic dyes*.

(*a*) *Aniline black.*—This term is applied to the insoluble black pigment which is produced by the oxidation of aniline in acid solution. In 1834 Runge noticed that a blue-black compound was produced by oxidising aniline with chromic acid, but Wilm, in 1860, first described the formation of the product on the cotton fibre. The first successful process for producing aniline black on the fibre was patented by Lightfoot, in 1863. He used potassium chlorate and cupric chloride as oxidising agents, and the black proved to be of such excellent fastness that innumerable modifications of the process have since been proposed, and the literature of the subject is very extensive.

Numerous oxidising agents have been employed in the production of aniline black, *e.g.* chlorates, chromates, salts of copper, vanadium, tungsten, cerium, &c. Aniline black may also be produced by electrolytic (Goppelsröder, Jahresber. 1876, 702) or by atmospheric (Green, J. Soc. Dyers, 1908, 231) oxidation.

Pure aniline on oxidation yields a blue-black, the homologues and allied compounds giving somewhat different shades ; *e.g.* orthotoluidine produces a brownish-black, paraphenylene diamine a deep black, and para-aminodiphenyl-amine (diphenyl base) a greenish black. The oxidation of a-naphthylamine on the fibre results in the formation of *naphthylamine violet*, but this colour is not of much importance.

The composition of aniline black has been the subject of much investigation (*see* Armand Müller, Chem. Zentr. 1871, 288 ; Goppelsröder, Jahresber. 1876, 702 ; Nietzki, Ber. 1878, 1094 ; Caro. Verhandt. d. Ges. Deutscher Naturforchen u. Arzte, 1896, 119 ; Willstätter and Moore, Ber. 1907, 2665 ; Marsden, J. Soc. Dyers, 1908, 9 ; Willstatter and Moore, Ber. 1909, 4118 ; Green and Woodhead, Chem. Soc. Trans. 1910, 223).

Three chief and successive products of the oxidation of aniline may be distinguished—*emeraldine, nigraniline,* and *ungreenable black*.

Emeraldine is produced by the limited oxidation of aniline, several residues linking up to form a chain of 4 molecules (Willstatter and Moore) or a chain or ring of 8 molecules (A. G. Green). The aniline residues are in all probability linked by nitrogen atoms in para- position, since para- compounds only have been obtained on oxidation or reduction.

Emeraldine is a greyish-green body which is always formed during the early stages of the production of aniline black. By the action of oxidising agents, it is converted into nigraniline and by the action of reducing agents it forms first proto emeraldine by addition of two atoms, and then leuco-emeraldine by addition of four atoms of hydrogen (Green, Chem. Soc. Trans 1910, 223). More powerful reducing agents split the molecule and produce amino- and para diamino-compounds or quinone.

Nigraniline, the second oxidation product of aniline, appears to contain eight aniline residues, and is said to be produced either by removal of two hydrogen atoms from the emeraldine molecule (Green) or by polymerisation with loss of hydrogen (Willstatter and Moore).

Nigraniline or aniline black is a violet-black body which is unaffected by alkalis, but which is turned green by mild reducing agents (sulphurous acid). owing to its reconversion into emeraldine. Dilute mineral acid also brings about indirectly the production of emeraldine from nigraniline. Oxidation of a portion of the latter substance probably takes place at the expense of the reduction of other molecules, since both quinone and emeraldine are formed in the reaction.

Ungreenable black, the final product in the technical formation of aniline black, is produced by the further oxidation of nigraniline in presence of aniline. It is a very stable body, and is not readily attacked by acids, alkalis, oxidising or reducing agents. Powerful oxidising agents, however, convert it almost quantitatively into quinone, and powerful reducing agents into a brown leuco- compound which is reoxidised to the original black on exposure to air. The presence of free aniline is essential to the production of ungreenable black, which suggests that it is a condensation product of emeraldine and aniline.

Technical production of aniline black.—Of the large number of modifications of Lightfoot's original process which have been suggested, very few have withstood the test of practical experience. The following technical methods may be distinguished : (1) *dyed blacks* ; (2) *aged blacks* ; (3) *steam blacks.*

(1) *Dyed blacks,* also known as *one-bath blacks,* are used for the dyeing of cotton yarn, which is often previously dyed in a sulphide black

vat. The ingredients used are (e.g.) aniline (12 lbs.), hydrochloric acid (18 lbs.), sulphuric acid (24 lbs.), and sodium dichromate (24 lbs.), in 40 gallons of water. The use of hydrochloric acid alone produces a bluish-black, and sulphuric acid alone a reddish-black, the mixed acids yielding a jet black.

The yarn is worked in the solution whilst slowly heating to the boiling-point, and the bronzy black thus produced is steamed to convert it into a good black which is ungreenable. This process does not tender the cotton. Many modifications of the process are used.

(2) *Aged blacks* are obtained by padding (saturating) the cotton with a solution containing aniline salt, some oxidising agent (sodium chlorate) and an oxygen carrier (copper sulphate, or vanadium chloride), after which the fabric is dried and 'aged'; the colour being developed by passing through an ageing chamber in which a moist atmosphere and a temperature of about 45° are maintained. The padded cotton has a green colour (emeraldine) which turns black (nigraniline) during ageing. The final change to ungreenable black is brought about by working the fabric in a solution of sodium dichromate.

Copper aged blacks are very largely produced on cotton piece goods by a process which differs only in detail from Lightfoot's original process.

Vanadium blacks are chiefly used in calico printing. Lightfoot (Bull. Soc. Ind. de Mulhouse, 1871, 285) first noticed the special efficiency of vanadium salts as oxygen carriers in the production of aniline black, and Witz (Bull. Soc. Ind. de Rouen, 1876, 310) showed that 1 part of vanadium chloride was sufficient to convert 40,000 parts aniline into aniline black.

The production of aged blacks is liable to tender the cotton unless the process is very carefully controlled.

Air oxidation black.—A. G. Green (J. Soc. Dyers, 1909, 191) has introduced an aniline black process in which atmospheric oxygen is the oxidising agent; some carrier such as cuprous chloride being present. The mineral acid usually employed is also replaced by formic acid, and by these modifications the liability to tendering of the fibre is greatly reduced.

The process is based on the fact that aniline oxidises much more rapidly in presence of a small quantity of a paradiamine or a para-aminophenol.

After padding, the goods are dried, aged, and chromed as in the case of the ordinary aged black.

(3) *Steam blacks* are more costly than aged blacks, but safer as regards tendering of the fibre. They are produced by padding with an aniline solution which contains sodium chlorate as oxidising agent, and sodium ferrocyanide as oxygen carrier. After padding, the goods are dried, steamed, and chromed. Lightfoot's original steam black only differed from this in that it contained potassium ferricyanide in place of the less expensive sodium chlorate and ferrocyanide.

Aniline black, when successfully dyed on cotton, is the fastest and most intense black which it is possible to produce. Its chief drawbacks are the tendency to turn green and the liability to tendering of the fibre, unless great experience and close supervision are exercised.

Application of aniline black to wool and silk. —The animal fibres are rarely dyed aniline black.

The black may be produced on silk by the same methods as on cotton, but the process is chiefly confined to the silk-cotton union material used as umbrella cloth.

Aniline black does not readily develop on wool, but if the wool is previously chlorinated (Lightfoot) or boiled with a mineral acid (Bethmann, Eng. Pat. 21236, 1901); the aged black may be produced. It is rarely met with.

(b) *The insoluble azo- dyes.*—The sulphonated azo- dyes which are so largely used in the dyeing of wool and silk have little or no affinity for cotton. Azo- compounds, however, may be produced on cotton by impregnating the fibre with one of the constituents, and then passing it into a solution of the necessary combining body. The non-sulphonated compounds are used in this process, and the insoluble dyes thus obtained are, in many cases, useful colours.

The constituent parts of an azo- dye are (a) a phenol or amine, and (b) a diazotised base; and the process (introduced by Holliday, in 1880) consists in saturating the cotton with an alkaline solution of a phenol, drying, and then developing in a solution of the diazotised base.

In calico printing (rarely in dyeing) the fibre may be impregnated with a paste containing the whole of the colour ingredients, and the colour developed by steaming.

Substances employed in the process : Phenols. —The only phenols practically employed in the padding operation are β-naphthol and β-oxynaphthoic acid anilid (naphthol AS). Amines are not used.

Aromatic bases.—The following list gives the principal bases employed and the colours they produce when combined with β-naphthol :—

Base	Colour produced with β-naphthol
Aniline	Orange yellow
Paranitraniline	Red (with copper, brown)
Paratoluidine	Yellow orange
Nitroparatoluidine	Orange
Xylidine	Red
Cumidine	Bluish-scarlet
Phenetidine	Scarlet
α-Naphthylamine	Blue shade of claret red
Aminoazobenzene	Crimson
Benzidine	Purplish-brown
Tolidine	Reddish-brown
Dianisidine	Blue (with copper)
Azo-black base	Black

Padding or grounding.—The intensity of the ultimate colour depends entirely upon the concentration of the padding solution, which, for a shade of medium strength may contain, per litre, 25 grams β-naphthol, 45 grams sodium hydroxide solution 36°Tw., and 75 grams Turkey-red oil. Cotton is evenly saturated in the cold with this solution, then dried at a low temperature and developed.

The developing process.—The most important dye produced by this process is *paranitraniline red*, which is dyed on a very large scale and used as a substitute for Turkey-red. The diazo-solution is prepared as follows : stir to a paste 10 lbs. paranitraniline with 2 gallons water ; then add 2 gallons hydrochloric acid (35°Tw.) and 6 gallons water. After mixing well, add 5½ lbs. sodium nitrite dissolved in 2 gallons water. Dilute to 200 gallons, and add sodium

acetate to neutralise the excess of hydrochloric acid. The colour is produced instantaneously on passing the padded cotton into this solution, the cotton being subsequently washed, dried, and soaped.

Various stable forms of the diazotised base appear under the names azophor red, nitrazol, and nitrosamine red.

Azo-oranges, yellows, crimsons, claret-reds, &c., are obtained in a similar manner by the use of the various bases given in the above table.

Azo-browns are produced by adding an alkaline solution of copper to the β-naphthol prepare, and developing with paramitranilme or β-naphthylamine.

Azo-blues are obtained by padding with β-naphthol, developing with dianisidine, and subsequently treating with cupric chloride and chromic acid.

(c) *The metallic dyes* : *Iron buff and Nankin yellow.*—These two colours, which differ only in depth of shade, are produced by precipitating hydrated ferric oxide on the fibre. They are dyed chiefly on cotton, and produce yellow to light-brown colours which are fast to light, washing, or alkalis, but are readily attacked by acids. The cotton is padded in a solution of a ferrous or ferric salt, and then passed into an alkaline solution. If the cotton is previously mordanted with tannin, more even shades are produced, the black tannate of iron being subsequently destroyed by a treatment with sodium peroxide (Knecht) or other oxidising agent. Iron buff is only produced on wool or silk as an intermediate product in dyeing Prussian blue.

Manganese bronze.—This colour is produced on cotton by precipitating manganous hydroxide on the fibre, and oxidising this to the brown manganic peroxide.

Chrome yellow is produced on cotton by impregnating with a solution of lead acetate, drying, and passing into a solution of potassium dichromate.

Chrome orange—This compound is a mixture of normal lead chromate (chrome yellow) and basic chromate. It is obtained by treating cotton dyed chrome yellow with lime water.

Prussian blue is produced on cotton by first dyeing an iron buff, and then passing into an acid solution of potassium ferrocyanide. This colour is extremely fast to light, but is sensitive to alkalis. It is produced on silk in a similar manner as a constituent in dyeing that fibre black. Prussian blue is little used on wool, but is readily produced either by a process analogous to the above, or by making use of the fact that when heated in acid solution with wool, the prussiates undergo decomposition with formation of Prussian blue.

COLOURING MATTERS USED IN DYEING.

Natural dyestuffs : *Indigo.*—There are two distinct methods of applying indigo in dyeing, and the most important, the vat method, has already been described (*v.* Vat *dyes*, p. 586). Indigo may also be used as an acid dyestuff by converting it into the disulphonic acid. This sulphonic acid is known as indigo carmine or indigo extract. It dyes a brighter blue shade than vat indigo, but it is much less fast to light and washing. It is largely used on wool and silk, but is inapplicable to cotton.

Logwood is a mordant dyestuff and is used for all fibres. On *wool* it is largely employed for producing blacks, and in conjunction with other dyestuffs for browns, olives, greys, &c.

Potassium or sodium dichromate is the usual mordant, but a single-bath logwood black may be produced by using a mixture of logwood, ferrous sulphate, and oxalic acid. Logwood is now chiefly employed in the form of unoxidised (for cotton) or oxidised (for wool) extract. On *silk* and *cotton*, logwood is only used for black dyeing.

Brazilwood, peachwood, and Limawood constitute the class of soluble red woods. They are now very little employed, the colours they produce being fugitive to light. They produce reds with aluminium, reddish-browns with chromium, and purples with iron mordants.

Camwood, barwood, and sanderswood are known as the insoluble red woods. If wool is boiled with the ground wood, it acquires a reddish-brown colour, which is still employed as a ' bottom ' for indigo vat blue. They are, however, mordant dyestuffs, producing brownish reds with chrome mordant.

Madder.—This dyestuff, once of great importance, has now been almost entirely superseded by synthetic alizarin. It is still used to a limited extent in the dyeing of wool felt, since it penetrates through the material more readily than alizarin. With chromium mordant it gives a reddish-brown ; with aluminium a red, and with iron a purple shade. The use of madder in the woad vat has already been referred to (*v.* Vat *dyes*). This dyestuff is not now used on cotton or silk.

Cochineal.—The use of this valuable dyestuff in dyeing is now confined to the production of scarlet shades on woollen cloth, for which purpose considerable quantities are still imported. Stannous chloride is the mordant employed, and the colour is produced by the one-bath method. The aluminium and tin lakes are used as pigments in painting and printing.

Lac-dye may be employed in the same way as cochineal, and gives similar shades. Since the commercial product contains a considerable amount of mineral matter, the ground dyestuff is treated with dilute hydrochloric acid before use.

Cudbear and orchil (or *archil*).—These products are essentially the same dyestuff, the former in the solid and the latter in the condition of paste. It is one of the few natural colouring matters which dye wool without a mordant. Wool and silk may be dyed in a neutral, slightly acid, or slightly alkaline, solution. It produces full, rich crimsons, and is still used to a considerable extent. The colouring matter is not applicable to cotton.

Safflower was formerly much used in dyeing bright pinks upon cotton, but is now obsolete as a dyestuff.

Annatto produces orange shades on silk without a mordant ; it is applied in a hot soap-bath. Annatto is still used in colouring cheese and butter.

Weld.—This mordant dyestuff produces pure yellows in conjunction with aluminium mordant. When used as a ' topping ' for indigo vat blue, a special shade of green, known as ' carriage green,' is obtained.

Fustic is the most important of the natural yellow dyewoods, and is still employed in

conjunction with chrome mordant on wool as the yellow constituent in compound browns, olives, greys, &c. It is chiefly used in the form of fustic extract.

Osage orange is closely allied to fustic. Its utilisation as a dyestuff is only of recent date and is confined to America.

Quercitron bark and flavin are also natural yellow mordant dyes, producing somewhat brighter shades than fustic, but are now obsolete.

Persian berries.—This mordant dyestuff is employed by the calico printer for producing bright orange shades with tin mordant.

Turmeric is the only representative of the natural colouring matters which acts as a direct dye towards cotton, silk, and wool. It produces yellow shades, which are brighter if dyed in a bath acidified with alum.

Catechu, cutch, and gambier.—These dyestuffs are still largely employed in cotton dyeing. The cotton is steeped in a strong solution of the dye, and attracts the colouring matter. The cotton is then passed into a boiling solution of potassium dichromate, which, by oxidation, produces insoluble brown japonic acid upon the fibre. A little copper sulphate is frequently added to the catechu bath, whereby fuller and faster shades are produced.

Silk is dyed in a similar manner for the production of weighted blacks, the chromium, fixed during the oxidising process, subsequently acting as a mordant for logwood.

Other natural dyestuffs.—Colouring matters are very widely distributed in the vegetable kingdom, and all countries where the textile arts have attained any great development (notably India, Persia, and Japan) had until recently each its own series of indigenous products which were used as dyestuffs. In Donegal, Sutherland, and other localities, the homespun tweeds, &c, are still largely dyed by means of the various lichens, roots, barks, nuts, &c., found in the neighbourhood.

Synthetic dyestuffs. The number of individual synthetic dyestuffs now at the dyer's disposal is very large, and includes dyes yielding all possible hues. There is infinite variety in the characteristics of the various artificial dyes, and in most cases it is not difficult to match a given shade or to comply with given conditions as regards properties. Being, therefore, more convenient to use, and in very many cases cheaper and faster than the natural dyestuffs, the latter have been largely superseded.

The dyeing properties and the characteristics of the dyed colours depend chiefly upon the chemical groups to which the dyes belong, but, as indicated in the section dealing with the classification of dyes, the chemical groups do not coincide with groups based on the method of application (*v. Classification of colouring matters,* p. 575).

(1) *Nitroso colouring matters.*—This class includes fast-green or dark-green and naphthol-green. In conjunction with iron mordants, both these dyestuffs give olive-green colours remarkable for their fastness to light.

Cotton is dyed with dark-green by mordanting with iron, and dyeing in a neutral bath. Wool is mordanted with ferrous sulphate and oxalic acid, and dyed in a neutral bath. Silk is dyed in a similar manner.

Naphthol green which contains iron as a constituent is only applicable to the animal fibres. Wool is dyed with the addition of sulphuric acid.

(2) *Nitro-colouring matters.*—The most important members of this class are : picric acid, Victoria orange, aurantia, palatine orange, naphthaline yellow, naphthol yellow. These colouring matters are only applicable to the animal fibres, which are dyed in a bath slightly acidified with sulphuric acid. The colours they yield are not fast to light. Picric acid yellow is remarkable for its extreme freedom from any trace of orange. On exposure to light it rapidly becomes brownish, owing to reduction of the nitro groups.

(3) *The azo- group.*—These may be divided into monazo, disazo, trisazo, and tetrakisazo-dyes, according to the number of azo- groups they contain. They may be further classified into aminoazo- (NH_2) and oxyazo- (OH) dyes, and into other subdivisions based upon the state of combination of the azo- group. A few of the azo- colours are basic dyes ; a large number of the acid dyes, and acid-mordant dyes, belong to this group, and practically the whole of the direct dyes. The azo- dyes vary greatly in their degree of fastness to light, and in other properties.

(4) *The di- and tri-phenylmethane group.*—This group includes most of the basic dyes, such as auramine, magenta, methyl violet, malachite green, &c. These bodies, when sulphonated, form acid dyes, and therefore such dyestuffs as acid magenta, guinea green, &c., and also patent blue, Victoria blue, fall under this group. As a class, these dyestuffs are fugitive to light.

(5) *The oxyketone group.*—This group includes most of the artificial mordant dyes ; *e.g.* the alizarin reds, yellows, blues, browns, &c. Most of the dyestuffs of this group are extremely fast to light and other influences, which renders them of the greatest importance.

(6) *The pyronine group.*—This includes (1) the pyronines proper, a small class of basic dyes, of which pyronine red is an example ; (2) the much more important group of the phthaleins. The latter includes both basic and acid rhodamines, the eosins and the mordant dyestuffs gallein and cœrulein.

(7) *The acridine group.*—This includes a few basic dyestuffs of which the chief is **acridine** orange.

(8 and 9) *The oxazine and thiazine group.*—This group also includes both acid (thiocarmine), basic (methylene blue), and mordant dyes (gallocyanin).

(10) *The azine group* includes the valuable basic dyes the safranines, and the basic and acid indulines and nigrosines.

The dyeing of mixed fabrics of cotton and wool may be carried out by selecting those colouring matters for which both fibres have an attraction, *e.g.* the benzidine dyes, &c., or by first dyeing the wool in the usual manner with an acid colouring matter, then mordanting the cotton with tannic acid and tartar emetic or stannic chloride, and dyeing in the cold with a basic colouring matter. The so-called 'cross-dyeing' process is carried out by first dyeing the cotton (usually with sulphide or other 'fast' dyes) in warp form, then weaving with a

wool weft and dyeing the latter by means of acid dyes. Logwood blacks on union are dyed by first mordanting the cotton in the cold with myrobolans and nitrate of iron, then the wool with a boiling solution of potassium dichromate, and finally dyeing both fibres thus mordanted in a hot decoction of logwood. Mixtures of cotton and silk are dyed by methods similar to those employed for cotton and wool. Fabrics of wool and silk are dyed by methods similar to those usual for wool or silk alone.

When dyeing *compound shades*, the main principle to be observed is to apply simultaneously only such colouring matters as are applicable, when used singly, by methods as similar as possible to each other. Basic and acid colouring matters ought not to be applied together in the same dye-bath, since the one requires a neutral, the other an acid, bath in order to yield their full colouring power. Basic colouring matters, however, may be quite well applied to mordanted cloth along with phenolic colouring matters, since both these classes usually dye in a neutral bath.

It is very irrational to produce compound shades by the application of a mixture of fast and fugitive colours ; the best results are obtained by employing colouring matters of about equal fastness to various influences. If this rule is not observed, the dyed colour is liable to change materially in shade under those influences to which it is subsequently submitted, e.g. light, washing, &c.

For further information on the subject of dyeing, the following works may be consulted :—

1813. The Philosophy of Permanent Colours E. Bancroft.
1835–1861. Recherches chimique sur la Teinture. E. Chevreul.
1869. Dictionary of Dyeing and Calico-printing. C. O'Neill.
1874. A Practical Handbook of Dyeing and Calico-printing. W. Crookes.
1876. Dyeing and Calico-printing. F. C. Calvert.
1885. The Dyeing of Textile Fabrics. J. J. Hummel.
1893. La Pratique du Teinturier. Vol. 1, 1893 ; Vol. 2, 1894 ; Vol. 3, 1897. J. Garçon.
1901. Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico-printing. C. Rawson, W. M. Gardner, and W. F. Laycock.
1903. Theorie und Praxis der Modernen Färberei. A. Ganswindt.
1904 *et seq.* Systematic Survey of the Organic Colouring Matters. G. Schultz and P. Julius, transl. by A. G. Green.
1907. Färbereichem. Untersuchungen Anleitung zur Untersuchung und Bewertung der wichtigsten Färberei, Bleicherei, Druckerei, und Appretur-Materialien. 2nd edit. P. Heermann.
Étude sur les Industries du Blanchiment, de la Teinture, de l'Impression. O. Picquet.
1910. A Manual of Dyeing. 2nd edit. E. Knecht, C. Rawson, and R. Loewenthal.
Identification of the Commercial Dyestuffs. Mulliken.

1912. Bleaching and Dyeing of Vegetable Fibrous Materials. J. Hübner.
Färbestofftabellen. G. Schultz.
Mercerisation und Appretur. P. Gardner.
L'Industrie des Matières Colorantes Organiques. A. Wahl.
1913. Synthetic Dyestuffs and Intermediate Products from which they are derived. 2nd edit. J. C. Cain and J. F. Thorpe.
1915. The British Coal-tar Colour Industry. W. M. Gardner.
The Analysis of Dyestuffs. A. G. Green. W. M. G.

DYESTUFFS, IDENTIFICATION OF, ON FABRICS. The recognition of the particular dyestuff which has been employed in dyeing a fabric is frequently a matter of considerable difficulty. If one dyestuff only has been used, it may be possible to identify it with little trouble, but when, as is often the case, two or more dyes have been employed to produce a given colour, their separation and recognition may be a very complex problem.

In the identification of dyestuffs, the ordinary basis of qualitative analysis is as far as possible made use of, i.e. the *group* to which the colouring matter belongs is first determined, and then tests are applied to identify it as an individual substance. There are, however, such a large number of closely related compounds amongst the dyestuffs, many being isomeric, and differing only (e g.) in the position of a sulpho- group, that with the small amount of substance frequently at disposal it is quite impossible to definitely identify a specific commercial product This is, however, of minor importance.

The recognition of a dyestuff is much facilitated by a knowledge of the dyeing properties of the various groups of colouring matters. In a given case this may greatly limit the possibilities. For example, no one with a knowledge of dyeing processes would search for a cochineal scarlet on cotton or a paranitraniline red on wool. The presence or absence of certain metallic bases in the ash of the incinerated material is also a useful indication of the nature of the dyestuff under investigation, and an examination of this point should be made.

What may be termed the ' dyeing groups ' of colouring matters do not coincide with the ' chemical groups.' For example, the dyeing group of ' basic ' dyes, the members of which are fixed on cotton by means of a tannin mordant, includes members of the triphenyl methane, azine, azo-, acridine, and other chemical groups.

To determine the dyeing group to which a colouring matter present on a fabric belongs, acid and alkaline solvents are used as ' stripping ' agents. The following are the general reactions :

ACTION OF 'STRIPPING AGENTS.'

Dyeing group	Stripping solution
Mordant dyes	50 c.c. HCl (conc.) per litre
Basic dyes on wool	5 p.c. acetic acid
„ „ on cotton	3 p.c. sodium hydroxide
	3 p.c. ammonia 0·880 s.g.
Acid dyes ⎫	A small piece of mer-
Direct cotton dyes ⎭	cerised cotton is placed in the solution.

In each case the fabric is boiled for 5 minutes in the solution.

With direct cotton dyes the small piece of white cotton placed in the solution becomes dyed. With acid dyes this does not occur.

The action of the above stripping agents can only be considered as general in regard to a particular group, and many exceptions will be found in dealing with particular members of the group, e.g. some acid dyes are only slightly stripped by boiling in dilute ammonia, and a few of them stain mercerised cotton. Too much reliance must not, therefore, be placed on these stripping reactions.

The most satisfactory group reagents for classifying dyestuffs into the chemical groups are acid or alkaline reducing agents ; on the use of which several schemes of identification have been based. These reagents were first proposed by Witt, in 1886, whose scheme was extended by Weingaertner, in 1887 ; but the systematic development of the scheme of analysis is mainly due to A. G. Green.

The reactions of dyestuffs are considerably influenced by the nature of the fibre upon which they have been fixed, which also determines the particular dyeing process necessary. For example, the basic colours dye wool and silk direct, whereas their fixation on cotton involves the use of a tannin mordant. It is convenient, therefore, to treat separately the identification of dyestuffs on animal and on vegetable fibres.

Identification of dyestuffs on wool.—Tables for the identification of dyestuffs on wool have been published in Hummel's Dyeing of Textile Fabrics ; in Knecht, Rawson, and Loewenthal's Manual of Dyeing ; in Lehne's Färber Zeitung, and by many other authors ; but the most systematic and reliable scheme is that of Green (Analysis of Dyestuffs, 2nd edit. 1915). In this scheme, which is now to be described, the dyeing groups are first distinguished by the action of suitable solvents, and then further differentiation is carried out by the use of reducing agents with subsequent reoxidation. The various groups of dyestuffs as dyed on animal fibres, show the following reactions :—

| Decolourised by hydrosulphite | | | | Not decolourised, but changed in |
Colour restored on exposure to air	Colour not restored by air, but restored on oxidation with persulphate	Colour not restored either by air or persulphate	Not altered by hydrosulphite	shade. Original colour restored by air or persulphate
Azines, oxazines, thiazines, indigoids	Triphenyl-methane group	Nitro-, nitroso-, and azo- groups	Pyrone, acridine, quinoline, and thiazol groups. Some members of the oxyketone group.	Most dyestuffs of the oxyketone group

In Green's scheme the following reagents are employed, and must be used of the strength indicated :—

Dilute ammonia (1 : 100) —1 c.c. conc. ammonia ; 100 c.c. distilled water.

Aqueous-alcoholic ammonia.—1 c.c. conc. ammonia ; 50 c.c. strong alcohol or methylated spirit ; 50 c.c. water.

Dilute acetic acid (5 p.c.).—5 c.c. glacial acetic acid ; 95 c.c. water.

Dilute alcohol (1 : 1).—50 c.c. strong alcohol or methylated spirit ; 50 c.c. water.

Dilute hydrochloric acid (1 : 10).—10 c.c. conc. hydrochloric acid ; 90 c.c. water.

Caustic soda (10 p.c.).—10 grams solid caustic soda in 100 c.c. of water.

Hydrosulphite AX.—Dissolve 50 grams hydrosulphite NF conc. or rongalite C, i.e. the formaldehyde compound of sodium sulphoxylate, in 150 c.c. of hot water. Add to the solution at 80°-90° 0·25 gram of precipitated anthraquinone previously ground to a paste with a little of the solution, and dilute the whole to 500 c.c. with cold water. The solution should be slightly alkaline. It may become acid on keeping.

Hydrosulphite B.—Dissolve 50 grams hydrosulphite NF conc. or rongalite C in 500 c.c. water, and acidify with 2 c.c. of acetic acid. This is used only for yellows and oranges.

Persulphate.—A cold saturated solution of potassium persulphate, or a 1 p.c. solution of ammonium persulphate. If alkaline, neutralise carefully with acetic acid.

Sodium acetate (5 p.c.) —5 grams crystallised sodium acetate ; 100 c.c. distilled water.

Procedure.—The reactions are carried out in test-tubes upon pieces of the material about ¾-1 inch square, which are covered with about 1-1½ inches of the reagent. The tests should be carried out exactly as described. Except when specially stated, the reagents are to be applied in succession to fresh portions of the material. In making 'stripping tests,' the degree of stripping is judged by comparing the remaining depth of shade with that of the original pattern. The colour of the stripping solution cannot be relied upon as a guide. In boiling with dilute acetic acid and dilute ammonia, it is found advantageous to repeat the extraction, as a better stripping is thereby obtained, and with acid dyestuffs any staining of the cotton by the first strong extract is removed during the second boil. In testing with dilute ammonia or sodium acetate, the material is placed in a test-tube with a piece of white mercerised cotton cloth, somewhat smaller in size, and boiled for the time prescribed. If the shade is a pale one, the size of the sample should be increased and that of the cotton

diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables III. and VII.), as in these cases the acid dyestuffs are less easily extracted, and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed well under the tap, and allowed to lie on white paper. With most dyestuffs which form air-oxidisable leuco- compounds, the colour returns immediately or in a few minutes, but with others a longer time is required. The reaction is accelerated by exposing the pattern to ammonia vapour. If the colour does not return, the pattern is boiled with a little water in a test-tube, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as a nitro-, nitroso-, or azo- compound. The depth of the restored colour varies greatly in different cases ; with some dyestuffs the colour reappears with nearly its original depth, but with others (probably on account of the greater solubility of their leuco-compounds) only a pale shade may return. Safranine and its azo- derivatives are peculiar in yielding a violet colour on reoxidation of the leuco- compound, this being due to the condensation of the leuco-safranine with the formaldehyde present in the hydrosulphite NF.

The tables (I. to VII., pp. 596-602) give the scheme of analysis.

These tables do not always differentiate between closely related individual dyes, for which purpose further tests must be made At this stage of the investigation it is very desirable to procure small pieces of material dyed with such known colouring matters as the group tests, combined with the colour of the sample, have indicated as probable Parallel individual tests should then be applied with these and with the sample under examination.

The following series of reagents have been found by W. M. Gardner to be convenient for this purpose. They should be applied in the order given, and used as follows :—

Application of cold reagents.—Steep a piece of the material 1 by ½ inch in (say) 5 c.c. of reagent for 5 minutes in a small porcelain dish.

Application of reagents by boiling.—In a test-tube place 10 c.c. of reagent and a piece of material 1 by ½ inch. Boil *gently* for 3 minutes.

Application of nitric acid test.—On a white glazed porcelain plate, spot the material by dipping a glass rod into the acid and then pressing it on to the cloth. Note the changes in colour which occur during the formation of the spot, and re-examine after several hours, noting any further change.

Reagents for identifying individual dyestuffs :

1. Boiling water.
2. 5 p.c. acetic acid, boiling.
3. 3 p.c. ammonia, boiling.
4. 3 p.c. soap, boiling.
5. Boiling alcohol.
6. Concentrated sulphuric acid, cold.
7. 3 p.c. ammonium persulphate, cold.
8. Bleaching powder solution, 5°Tw., cold.

Use small pieces of white wool, silk, and cotton along with the dyed sample.

9. 50 grams $SnCl_2.2H_2O+100$ c.c. HCl. 32°Tw. per litre, cold.

10. 5 c.c. $NaNO_2$ (5 grams per litre), and 5 c.c. H_2SO_4 (3·5 grams per litre) boiling.

11. Apply test 10 cold, then wash and steep the material in a solution of sodium β-naphtholate 5 grams per litre.

12. Concentrated nitric acid (spot test).

If the sample under examination shows the same reactions as any one of the control samples, with each of the above reagents, its identity may be considered as clearly established.

Knecht (J. Soc. Dyers, 1904, 98) states that titanous chloride possesses advantages over both stannous chloride and sodium hydrosulphite as a test for dyestuffs. The solution is prepared by boiling together 25 c.c. commercial titanous chloride solution (20 p.c.) and 25 c.c. HCl, 32°Tw., and diluting to 1000 c.c. with water.

IDENTIFICATION OF DYESTUFFS ON COTTON.

Green (Analysis of Dyestuffs, 1915) has worked out an analytical scheme for the detection of dyestuffs on cotton on the same lines as that previously described for wool.

The reagents are as follows :—

1. *Dilute ammonia* —1 c.c. strong ammonia to 100 c.c. distilled water.

2. *Dilute caustic soda.*—10 grams caustic soda in 100 c c. water.

3 *Saline caustic soda* —10 c.c. caustic soda solution (35-40 p.c. NaOH) to 100 c.c. saturated solution of salt.

4. *Formic acid* 90 p.c.—Concentrated commercial acid.

5. *Dilute formic acid.*—1 c.c. formic acid (90 p c.) to 100 c.c. distilled water.

6. *Dilute hydrochloric acid.*—5 c.c. hydrochloric acid (30 p.c.) to 100 c.c. of water.

7. *Soap solution.*—10 grams soap in 300 c.c. of water.

8. *Tannin solution.*—10 grams tannic acid and 10 grams sodium acetate in 100 c.c. of water.

9. *Bleaching powder solution.*—Fresh solution at 5°Tw.

10. *Hydrosulphite AX* (same as for wool, see p. 593).

11. *Hydrosulphite B* (same as for wool, see p. 593).

12. *Hydrosulphite BX.*—Dissolve 50 grams of rongalite or hydrosulphite NF conc. in 125 c.c. of hot water. Grind 1 gram of anthraquinone (precipitated, not sublimed) to a fine powder, and reduce to a smooth paste with a little of the rongalite solution. Add this paste to the remaining solution, and heat the whole for 1 or 2 minutes at about 90°. Then dilute with cold water to 500 c.c., and, after standing until cold, add 1½ c.c. of glacial acetic acid. Keep in a well-stoppered bottle with greased stopper. The reagent should be tested occasionally by trying its effect on cotton dyed with α-naphthyl-amine bordeaux, which should be fully discharged after boiling for 1 or 2 minutes. The anthraquinone may be replaced by β-oxyanthra-quinone, which can be employed in the same way or previously dissolved in a little alcohol before it is added to the hydrosulphite. It has the advantage of giving a clearer solution, but is not so generally available.

13. *Persulphate solution.*—A cold saturated

solution of potassium persulphate, or a 1 p.c. solution of ammonium persulphate.

14. *Acid stannous chloride.*—100 grams stannous chloride to 100 c.c. hydrochloric acid (30 p.c.) and 50 c.c. water. The hydrochloric acid must be free from arsenic. In testing for sulphide colours, this reagent may be replaced with advantage by a strong solution of titanous chloride.

15. *Chromium fluoride reagent.*—A solution of 10 grams chromium fluoride and 5 grams sodium acetate in 100 c.c. water.

Procedure : General.—All the reactions are performed in test-tubes, with pieces of material about ½–¾ of an inch square, which are covered to the depth of from 1½ to 2 inches with the reagent. The degree of stripping is judged by comparing the remaining shade with that of the original pattern ; the colour of the stripping solution cannot be relied upon as a guide. In testing the colours of calico prints, the separate colours should be cut out and the reactions tried upon them separately. With cotton and wool, or cotton and silk unions, the weft is separated from the cotton warp, and each submitted to examination. Doubt may frequently exist as to how a particular shade should be classified, whether, for instance, a reddish-blue is to be regarded as a blue or a violet. In such cases the tables referring to both colours should be employed ; but since the same general scheme is adopted throughout the tables, this can scarcely give rise to confusion. The same remark applies to possible mixtures ; thus in examining a certain green shade, both the yellow and the blue tables may have to be used.

To distinguish between individual dyestuffs of the same group the same method should be adopted as in the case of wool (*see* p. 594).

It is obvious that in many instances the analytical procedure may be greatly simplified by exclusion of dyestuffs the presence of which is rendered improbable or impossible by the special circumstances of the case, *e.g.* by the material, shade, or mode of application of the colour.

Stripping test.—A few of the direct dyestuffs are partially stripped by dilute ammonia, and may thus give rise to the impression that they are acid colours. To avoid this error, it is advisable to add a small piece of white cotton when carrying out the test. With an acid dyestuff the cotton is either not tinted or becomes white on boiling a second time with dilute ammonia.

Transference of basic dyes to wool.—The tannin mordant is first removed, as in testing for a basic colour, by boiling the pattern for half a minute with saline caustic soda. It is then well washed to remove all alkali, and is boiled with a piece of white wool (half the size of the cotton or less) in a little water for 1 or 2 minutes. In most cases the dye base will leave the cotton almost entirely, and dye the wool a full shade. If the colour does not develop on the wool, one or two drops of dilute formic acid (1 : 100) may be added. In the case of a few dyestuffs which are more difficult to strip (*e.g.* basic greys), it is necessary to extract the colour with dilute hydrochloric acid (1 : 20), carefully neutralising the extract with ammonia before adding the wool.

Tannin test for basic dyes.—Add a few drops of tannin solution to the formic acid extract. Shake well, and if the precipitate does not form at once, allow to stand a few minutes. Some colouring matters such as the rhodamines, gallocyanines, and chrome colours of the rosaniline series (which contain carboxyl- or hydroxyl- groups in addition to basic groups) only precipitate slowly, and the precipitate, being more finely divided, is sometimes difficult to see.

Bleeding test for direct dyestuffs.—In testing for direct dyestuffs by the bleeding test, the sample is placed in a test-tube together with a smaller piece of white mercerised cotton cloth, and boiled with soap solution for about a minute. The soap solution may be replaced by a 5 p.c. solution of sodium carbonate.

Lead acetate test for sulphide dyes.—The sample is first boiled for two minutes with a 10 p.c. solution of sodium hydroxide to remove any adventitious sulphur compounds. It is then well washed and just covered with acid stannous chloride solution. The mouth of the test tube is closed by a cap of filter paper closely wrapped round it, into the centre of which is placed, by means of a glass rod, one drop of lead acetate solution. The contents of the test-tube are slowly heated to the boiling-point, when a blackish-brown stain of lead sulphide appears if a sulphide colour is present. The brown spot will again disappear on continued boiling on account of the decomposition of the lead sulphide by the hydrochloric acid evolved. It is important to pay special attention to the cleanliness of the test-tubes employed for this test, as tubes which have been previously used for hydrosulphite reductions acquire a thin invisible deposit of sulphur upon their walls, which, on boiling with stannous chloride, gives rise to hydrogen sulphide, and thus may lead to error.

Reduction and reoxidation tests.—The reduction with hydrosulphite BX is carried out by boiling the sample with the reagent for from a minute to a minute and a half. The azines, thiazines, oxazines, &c., and most of the azo-dyestuffs are fully reduced in about half a minute, but the insoluble azo- colours and some direct dyestuffs require longer boiling to complete their reduction. In testing the reoxidisability by air, the reduced sample may be exposed to the fumes of ammonia, which in many cases accelerates oxidation.

Tests for vat dyestuffs.—(*See* Green and Frank, J. Soc. Dyers, 1910, 83 ; and Grand-mougin, Tabellarische Uebersicht der Kupen-farbstoffe.)

The analytical tables worked out by Green for the identification of dyestuffs on vegetable fibres, are given on pp. 603–609, Tables VIII. to XIV.

S. T. Mulliken (Identification of the Commercial Dyestuffs, 1910) has published a systematic scheme of analysis, primarily intended for the examination of the dyestuffs in a substance. The tables give the reactions of 1475 distinct dyestuffs, and are of great service in the identification of dyes on the fibre.

Spectroscopic examination of dyestuffs.—The absorption spectra of dyestuffs may be used as an aid to their identification. In the second

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE III.—PURPLE AND VIOLET COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Test sequence	No.	Dyes
Little or no colour is stripped : Acid, Vat, Mordant, or Salt dyestuff. Boil twice for one minute with aqueous alcoholic ammonia (1 : 100) and hydrosulphite AX — **Little or no colour is stripped : Vat, Mordant, or Salt dyestuff.** Boil with hydrosulphite AX. — Colour changed to orange-brown or brown : **Alizarin class.** A mordant is present. Boil original fibre with dilute hydrochloric acid (1 : 10). — Fibre and solution red-brown to violet-brown	18	Alizarin bordeaux, alizarin claret, alizarin maroon.
Fibre and solution orange	17	Alizarin red S, &c., on Fe.
Decolourised. Colour is not restored either by air or by per-sulphate. **Azo class.** Test for a mordant (Cr) — Mordant absent : **Salt dyestuff.** Confirm by boiling with 5 p.c. sodium acetate and a piece of white cotton. Stained	16	Diamine, benzo, dianil, columbia, chlorazol, naphthamine, chlorantine, &c., violets.
Mordant present : **Acid-mordant dyestuff.**	15	Acid alizarin violet, acid chrome violet, eriochrome violet, Palatine chrome violet.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate . **Triphenyl-methane class.** A chrome mordant is present	14	Chromogene violet, metachrome violet, chrome violet
Decolourised. Colour returns to air. Test for a mordant — Mordant absent · **Indigoid Vat dyestuff.** Confirm by extraction with aniline and sublimation	13	Helindone violet, ciba violet, ciba heliotrope, thioindigo violet, &c.
Mordant present · **Azine, Oxazine, or Thiazine class.**	12	Gallocyanine, prune, celestine blue, correine.
Colour unaffected . **Pyrone class.** A chrome mordant is present	11	Galleine.
Much colour is stripped, but cotton remains white . Acid dyestuff. Boil with hydrosulphite AX. — Colour is changed to orange-yellow, restored by persulphate to a violet-brown · **Anthraquinone class**	10	Anthraquinone violet, alizarin direct violet, alizarin irisol, alizarin cyanol violet.
Decolourised. Colour is not restored either by air or by per-sulphate : **Azo class**	9	Lanacyl violet, azo acid violet, sulphon violet, Victoria violet erio fast purple, wool violet.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate : **Triphenyl-methane class.** — Little colour is stripped. Spot original fibre with conc. hydrochloric acid — Yellow spot	8	Acid violets, alkali violet, guinea violet, formyl violet, kitone violet, &c.
Pyrone classes. Boil with 5 p c. sodium acetate for one minute — Fibre unchanged	7	Pyrone colours, e.g., fast acid violets, violamines, and violet 4R, &c.
Fibre becomes reddish-brown	6	Red-shade soluble blues.
Much colour is stripped, but solution remains colourless. Treat original fibre with cold conc. sulphuric acid — Colour of fibre yellow to orange	5	Certain red-shade acid violets, e.g., acid violet 4RS and 5RS, red violets 4RS, &c.
Decolourised. Colour returns on exposure to air : **Azine, Oxazine, or Thiazine class**	4	Fast blue R, red shade indulines, &c.
Much colour is stripped : Basic dyestuff or Soluble Red Wood. Boil twice for one minute with dilute alcohol (1 : 1). — Unaffected. Al or Cr is present in ash. On boiling with dilute ammonia, the colour becomes much bluer	3	Soluble red woods, e.g., Brazilwood, Lima-wood, sapanwood, peachwood, &c.
Much colour is stripped : Basic dyestuff. Boil with Hydrosulphite AX — Decolourised. Colour does not return on exposure to air, but is restored by per-sulphate : **Triphenyl-methane class**	2	Methyl violet, ethyl violet, crystal violet, benzyl violet, brilliant violet, &c.
Decolourised. Colour returns on exposure to air : **Azine, Oxazine, or Thiazine class**	1	Neutral violet, rhoduline violet, methylene violet, tannin heliotrope, iris violet, &c.

RECOGNITION OF DYES ON WOOL OR SILK.
TABLE IV.—BLUE COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Little or no colour is stripped : Acid, Vat, Mordant, or Salt dyestuff. (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.

Boil twice for one minute with dilute ammonia

Little or no colour is stripped.—Vat, Mordant, or Salt dyestuff. Boil with hydrosulphite AX

Branch conditions	No.	Dyestuff
Colour changed to brown, becoming blue again on exposure to air :—**Alizarin class** Mordant present	26	Alizarin blue (Anthraquinoline class).
Decolourised. Colour is not restored either by air or by persulphate :—**Azo class**. Test for a mordant — Mordant absent :—**Salt dyestuff.** Confirm by boiling with 5 p.c. sodium acetate and a piece of white cotton. Cotton stained	25	Diamine, benzo, dianil, Chicago, chlorazol, naphthamine, &c., blues and sky blues, sulphon acid blue, sulphoncyanine, sulphonazurine, erio fast blue SWR, tolyl blue GR extra and 5R extra, &c.
Mordant present. Boil with 5 p.c. sodium acetate and a piece of white cotton for 2 or 3 minutes — Cotton is stained :—**Salt-mordant dyestuff**	24	Autochrome blue.
Cotton remains white :—**Acid-mordant dyestuff**	23	Chromotrope blue, acid chrome blue, chrome fast blue, anthracene chrome blue, fast mordant blue, salicine chrome blue, &c.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—**Triphenylmethane class.** Test for a mordant — Mordant absent	22½	Brilliant milling blue B.
Mordant present	21	Chrome blue.
Decolourised. Colour returns on exposure to air. Test for a mordant — Mordant absent. Treat fibre with aniline — Colourless solution :—**Pyrone dyestuff**	20	Fast acid blue R, violamine 3B.
Blue solution giving on evaporation a sublimable residue.—**Indigoid Vat dyestuff**	19	Indigo, helindone blue 3G and 2B, ciba blue, thioindigo blue, &c.
Mordant present :—**Anthra-quinone class.** Treat fibre with cold conc. sulphuric acid — Fibre and solution red	18	Eriochrome azurol, eriochrome cyanine, chrome worsted blue, chromal blue, chromoxane blue, &c.
Fibre and solution blue or violet	17	Gallocyanine, celestine blue, correine, prune, gallamine blue, delphine blue, brilliant delphine blue, indahzarin; lanoglaucine, ultra cyanine, ultra violet, &c.
Fibre and solution green	16	Brilliant alizarin blue, mercerol brilliant blue, indochromine, &c.
Mordant absent	15	Indanthrene blue WB.
Mordant present	14	Alizarin cyanine, brilliant alizarin cyanine, anthracene blue, alizarin indigo blue, acid alizarin blue 2B and GR, &c.

Much colour is stripped, but cotton remains white :—Acid dyestuff. Boil with hydrosulphite AX

Branch conditions	No.	Dyestuff
Colour un-affected, or slightly dark-er :—**Anthra-quinone class.** Fibre is not de-colourised, but colour changes — **Anthraquinone class.** Colour of re-duced fibre is — bright yellow to orange-brown, returning with persulphate	13	Alizarin astrol, alizarin uranol, cyananthrol, alizarin direct blue B, alizarin cyanol B, alizarin sky blue, anthraquinone blue, &c.
red-violet, returning with persulphate	12	Alizarin saphirol, anthracyanine, alizarin direct blue EB and E3B, alizarin cyanol EF, brilliant anthrazurol, eriocyanine LM, fast sky blue, &c.
Decolourised. Colour is not restored either by air or by persulphate.—**Azo class**	11	Lanacyl blue, azo acid blue, azo merino blue, azo navy blue, chromazone blue, azocyanine, &c.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—**Triphenyl-methane class** — Ammoniacal extract is colourless, but becomes blue on acidifying	10	Soluble blue, water blue, alkali blue, chlorazol brilliant blue 14B, isamine blue 8B, dianil blue 6G, brilliant sky blue 8G, &c.
Ammoniacal extract is blue. Treat fibre with cold conc. sulphuric acid — Fibre and solution colourless to pale yellow	9	Patent blue, new patent blue, Neptune blue, xylene blue, brilliant acid blue, kitone blue, erioglaucine, eriocyanine, eriochlorine, cyanole, cyanine, fast acid violet 10B, cyanogene, &c.
Fibre and solution red-brown to orange-brown	8	Wool blue, cyanole FF, intensive blue, &c.
Decolourised. Colour returns on exposure to air.—**Azine, Oxazine, Thiazine, and Indigo classes. Also Prussian blue** — The ammoniacal extract is colourless. Fe is present in ash	7	Prussian blue.
The ammoniacal extract is blue. On adding caustic soda — becomes violet on heating	6	Thiocarmine, fast blue, induline, acid cyanine, fluorescent blue, lazuline blue, &c.
at once becomes yellow	5	Indigo extract, indigo carmine.

Much colour is stripped :—Basic dyestuff. Boil with dilute alcohol (1 : 1). Boil twice for one minute

Branch conditions	No.	Dyestuff
Unaffecte d. Al or Cr is present in ash. On spotting with hydrochloric acid the blue is changed to brick-red	4	Logwood blue.
Much colour is stripped :—Basic dyestuff. Boil with hydrosulphite AX — Decolourised. A violet colour returns on exposure to air :—**Safranine azo dyestuff**	3	Janus blue, diazine blue, indoine blue, Janus dark blue, naphthindone, &c.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—**Triphenylmethane class**	2	Night blue, Victoria blue, setocyanine, setoglaucine, turquoise blue, &c.
Decolourised. Colour returns on exposure to air :—**Azine, Oxazine, or Thiazine class**	1	Methylene blue, Nile blue, Capri blue, cresyl blue, Meldola's blue, new methylene blue, diphene blue, &c.

RECOGNITION OF DYES ON WOOL OR SILK.
TABLE V.—GREEN COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Branch	Condition	No.	Dyestuffs
Little or no colour is stripped:—Acid, Vat, Mordant, or Salt dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Little or no colour is stripped.—Vat, Mordant, or Salt dyestuff. Boil with hydrosulphite AX. Colour changed to orange or orange-brown: Alizarin class	Original colour does not return on exposure to air, but is restored by persulphate. A chrome mordant is present	18	Alizarin cyanine green, alizarin viridine, brilliant alizarin viridine, &c.
	Original colour returns on exposure to air. A mordant is present	17	Cœruleine, alizarin green S, alizarin dark, green W.
Decolourised. Colour is not restored either by air or by persulphate.—Azo or Nitroso class. Test for a mordant	Colour changed to red-violet. The original colour is restored by persulphate. A chrome mordant is present	16	Eriochrome verdone, acid alizarin green.
	Mordant absent:—Salt dyestuff. Confirm by boiling with 5 p.c. sodium acetate and a piece of white cotton	15	Diamine, benzo, diamil, Columbia, chlorazol, naphthamine, &c., greens.
Mordant present. Boil with 5 p.c. sodium acetate and a piece of white cotton for two or three minutes. Cotton is stained.—Salt-mordant dyestuff		14	Diamond green 2S, chrome patent green N, mercerol green, &c.
Cotton remains white. Boil original fibre with conc. hydrochloric acid	Colour of fibre unchanged, or bluer.—Azo class	13	Diamond green B and 3G, chromoxal green, Cyprus green, omega chrome green, eriochrome green H and L, acid chrome green, &c.
	Fibre and solution light brown.—Nitroso class	12	Naphthol green B, gambines, dioxine, chrome green G, &c.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate : Triphenylmethane class. A Cr mordant is present		11	Chromoxane green, chrome green, fast chrome green, &c.
Decolourised. Colour returns on exposure to air. Test for a mordant	Mordant absent.—Indigoid Vat dyestuff. Confirm by extraction with aniline and sublimation test	10	Ciba green G, helindone green G.
	Mordant present.—Oxazine or Thiazine class	9	Alizarin green B and G
Much colour is stripped, but cotton remains white:—Acid dyestuff. Boil with hydrosulphite AX. Fibre is not decolourised, but colour changes.—Anthraquinone group. Colour of reduced fibre is—	Orange, returning with persulphate to grey-green	8	Anthraquinone green, alizarin cyanine green, alizarin brilliant green, fast acid green RH, anthraquinone blue-green.
	Red-violet returning with persulphate to bluish-green	7	Alizarin emeraldol, alizarin direct green.
Decolourised. Colour is not restored either by air or by persulphate :—Azo class		6	Sulphon acid green, mixtures of an azo blue and yellow.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate —Triphenyl-methane class		5	Acid green, light green, guinea green, wool green, Neptune green, alkali fast green, cyanole fast green, erio green, brilliant milling green B, night green, &c.
Decolourised. Colour returns on exposure to air :—Azine, Oxazine, or Thiazine class		4	Azine green S.
Much colour is stripped:—Basic dyestuff. Boil with hydrosulphite AX. Decolourised. Colour does not return on exposure to air, but is restored by persulphate : Triphenyl methane class		3	Malachite green, brilliant green, fast green, setoglaucine, solid green, China green, new fast green, &c.
Decolourised. Original colour returns on exposure to air :—Azine, Oxazine, or Thiazine class		2	Methylene green, Capri green, azine green, fast green M, &c.
Decolourised. A dark violet colour returns on exposure to air :—Safranine Azo dyestuff		1	Janus green, diazine green.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE VI.—BROWN COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Much colour is stripped :— Basic dyestuff. Boil with hydrosulphite AX

- Decolourised. A violet colour returns on exposure to air : Safranine azo dyestuff
  - **1** Diazine brown.
- Decolourised. Colour is not restored either by air or by persulphate :— Azo class
  - **2** Bismarck brown, Janus brown, tannin brown.

Little or no colour is stripped.—Acid, Vat, Mordant, or Salt dyestuff. Boil twice for one minute with dilute ammonia (1 : 100)

- Much colour is stripped :—Acid dyestuff. On boiling with hydrosulphite AX, decolourised. Colour is not restored either by air or by persulphate :— Azo class
  - **3** Acid brown, fast brown, resorcin brown, guinea brown, solid brown, sulphon acid brown, Neptune brown, wool brown, &c.
- Decolourised. Colour returns on exposure to air. Boil with 5 p.c. sodium acetate and a piece of white cotton for two minutes
  - Cotton remains white.— Indigoid vat dyestuff
    - **4** Helindone brown, ciba brown, thioindigo brown, &c.
  - Cotton is stained.—Salt dyestuff stilbene class
    - **5** Mikado browns.
- Decolourised. Colour does not return on exposure to air, but is restored by persulphate
  - **6** Chromogen, oxychromine.

Little or no colour is stripped.—Vat, Mordant, or Salt dyestuff. Boil with hydrosulphite AX

- Decolourised. Colour is not restored either by air or by persulphate :— Azo group. Boil with 5 p.c. sodium acetate and a piece of white cotton for two minutes
  - Cotton remains white. Cr is present. Acid-mordant dyestuff
    - **7** Anthracene acid brown, acid alizarin brown, anthracene chromate brown, diamond brown, palatine chrome brown, salicine brown, metachrome brown, mercerol brown, &c. Also manganese brown (Mn in ash).
  - Cotton is stained. Cr may be present. Salt dyestuff
    - **8** Diamine, benzo, diamil, Columbia, Congo, naphthamine, toluylene, Hessian, &c., browns.

Colour of fibre unaltered. Boil with dilute hydrochloric acid (1 : 10)

- Colour is stripped. Cr present
  - **9** Anthragallol, anthracene brown, alizarin brown.
- Colour is not stripped. Cr and Cu present
  - **10** Cutch.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE VII.—BLACK AND GREY COLOURS.

Boll twice for one minute with 5 p.c. acetic acid

Little or no colour is stripped :—Acid, Mordant, or Salt dyestuff. Boll twice for one minute with aqueous alcoholic ammonia (1 : 100) and a piece of white cotton

Much colour is stripped :— Basic dyestuff	The colour is stripped :— Acid or Salt dyestuff		Little or no colour is stripped :—Mordant dyestuff. Boll for half a minute with dilute hydrochloric acid (1 : 10)							
	The cotton remains white :— Acid dyestuff. On boiling with hydrosulphite AX, the colour is permanently discharged	The cotton is stained :—Salt dyestuff. On boiling with hydrosulphite AX, the colour is permanently discharged	Fibre and solution crimson	Fibre and solution orange to pale brown	Fibre blue or blue-violet, solution crimson, Test for indigo by extraction, evaporation, and sublimation	Unaffected. Treat original fibre with cold conc. sulphuric acid	Fibre unaffected.	Boll with hydrosulphite AX		Colour changed to brown. Original colour returns slowly on exposure to air
							Blue solution	Colourless solution	The colour is discharged. Boll for one minute with 5 p.c. sodium acetate and a piece of white cotton	
									Cotton remains white	Cotton is stained	
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Janus black, diazine black, jute black, methylene grey, new fast grey, &c.	Naphthol black, naphthylamine black, nerol, azo acid black, Palatine black, sulphocyanine black, sulphon black, Biebrich patent black, cresol black, &c.	Union black, Columbia, diamine, dianil, benzo, chlorazol, naphthamine, &c., blacks and fast blacks, direct deep black, direct blue black, &c.	Logwood on Cr.	Logwood on Fe, Bonsor's black.	A ' vatted black ' (indigo and logwood).	Alizarin cyanine black.	Aniline black.	Diamond black PV, PVB, P2B, F, diamond blue black EB, eriochrome black, eriochrome grey, chrome fast black, anthracene chrome black, acid alizarin black, fast chrome black, acid chrome black, &c.	Diamond black FB, FR, NG, GA, 2B, Palatine chrome black, anthracene acid black, alizarine black, monochrome grey, anthracene chromate grey, &c.	Naphthazarine, alizarin blue black SW, W, brilliant alizarin black, alizarin black S, WR, WX, &c.

RECOGNITION OF DYES ON VEGETABLE FIBRES

TABLE VIII.—YELLOW AND ORANGE COLOURS.

Boil with weak ammonia (1 : 100)

Condition (ammonia)	Branch 2	Branch 3	Branch 4	Branch 5	Branch 6	No.	Dyestuff
The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water, and boil with water and one or two drops of weak formic acid (1 : 100)	A coloured acid extract not precipitable by tannin. Reduce the original dyestuff with hydrosulphite BX	The colour is unaffected or changed in shade, becoming lighter, browner, or bluer. If altered in shade, exposure to air restores the original colour. Apply the lead acetate test	No H₂S is evolved. Boil with soap solution and white mercerised cotton	The white cotton is not stained.—Mordant or vat dyestuff. Boil with 90 p.c. formic acid. Also test ash for metallic mordant	Colour not stripped by formic acid. No mordant in ash :—Vat dyestuff	18	Helindone orange R, helindone yellow 3G, anthraflavone G, algole yellow 3G and R, algole orange R, indanthrene yellow, indanthrene orange RT and golden orange, indanthrene copper, cibanone yellow R and orange R.
					Colour stripped by formic acid. Al or Cr in ash.—Mordant dyestuff	17	Persian berries on Al or Cr mordants, alizarin orange on Al mordant.
				The white cotton is stained.—Thiazol salt dyestuff		16	Chlorophenine, chloramine yellow, diamine fast yellow B, FF, and C, Clayton yellow, thiazol yellow, thioflavine S, &c. Primuline developed with hypochlorite.
			H₂S is evolved :—Sulphide dyestuff			15	Yellows and oranges of the immedial, katigene, cross-dye, pyrogene, thiogene, sulphur, thional, &c., series.
		Decolourised or becomes light yellow. Original colour is not restored by air oxidation.—Azo dyestuff (including the Stilbene class) Boil with soap solution and white mercerised cotton	White cotton is not stained. Boil with pyridine	Colour is not stripped. Cr present in the ash :—Azo mordant dyestuff		14	Chrome orange, alizarin yellow R, GG, &c. diamond flavine, flavazol, &c.
				Colour is stripped :—Insoluble azo colour		13	Metamtranilne orange, nitrotoluidine orange, orange from naphthol AC.
			White cotton is stained :—Salt dyestuff	Fibre after reduction is colourless —Salt azo dyestuff		12	Chrysophenine, chrysamine, carbazol yellow, toluylene yellow and orange, stilbene yellows and oranges, benzo, Congo, diamine, and dianil yellows and oranges, pyramine orange, Pluto orange, &c.
				Fibre after reduction is light yellow and can be diazotised and developed red with betanaphthol.—Primuline azo-colour		11	Primuline developed with phenol or with resorcinol, cotton yellow G and R, oriol yellow, dianil yellow, &c.
	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution.—Basic dyestuff. Transfer to wool and boil with hydrosulphite B	Wool is permanently decolourised :—Azo class				10	Chrysoidine, tannin orange, Janus yellow, azo phosphine, new phosphine, &c.
		Wool is not decolourised. Boil cotton with hydrochloric acid (1 : 20)	Not decolourised. The conc. H₂SO₄ and alcoholic solutions are fluorescent.—Acridine class			9	Phosphine, benzoflavine, acridine yellow, rheonine, orange flavophosphine, &c.
			Decolourised			8	Auramine.
The colour is stripped. Boil with acidified water and small piece of white wool	Colour is transferred to the wool.—Acid dyestuff. Boil wool with hydrosulphite B	The colour is completely destroyed, both solutions and fibre being colourless. Treat original fibre with cold ammonium sulphide	Fibre is not blackened. Boil with hydrosulphite BX	Decolourised		7	Flavinduline.
				Not decolourised. Test for Al in ash	Al absent	6	Thioflavine T, methylene yellow, rhoduline yellow.
					Al present	5	Alizarin yellow A.
			Fibre blackened. Cr present in ash			4	Chrome yellow or chrome orange (lead chromate).
		Permanently decolourised :—Azo class				3	Indian yellow, orange IV., G, &c.
		Not decolourised :—Pyrone or quinoline class				2	Quinoline yellow, eosine orange.
	Colour not transferred to the wool. Sn is present in ash					1	Persian berries on tin mordant.

RECOGNITION OF DYES ON VEGETABLE FIBRES.

TABLE IX.—RED COLOURS.

Boil with weak ammonia (1 . 100)

The colour is not stripped. Boil for ¼ quarter of a minute with saline caustic soda, rinse with cold water, and boil for one minute with water and one or two drops of weak formic acid (1 : 100) Reduce original fibre with hydrosulphite BX		Cr absent:—**Anthracene Vat dyestuff** — Colour but little affected by formic acid	16	Algole red B, indanthrene red, indanthrene claret, ciba scarlet G.
		Cr in ash:—**Anthracene Mordant dyestuff** — Colour unaffected or changed to maroon or brown. Original colour restored on exposure to air.—Anthracene class. Boil with 90 p.c. formic acid. Also test ash for mordant	15	Alizarin, purpurines or alizarin maroon on Cr mordant.
		Colour stripped by formic acid. Al in ash:—**Anthracene Mordant dyestuff**	14	Turkey red, alizarin red, alizarin pink, alizarin maroon.
	A coloured acid extract precipitable by tannin is not obtained.	Colour changed to greenish yellow (not restored to original colour by air), which can be diazotised and developed red with betanaphthol :—**Primuline Azo colour**	13	Primuline developed with betanaphthol or with R-salt.
		No H₂S is evolved. Red vapours on heating :—**Indigoid vat dyestuff**	12	Algole red 5G and scarlet G, algole pink R, ciba red G and scarlet G, ciba bordeaux B, helindone red B and 3B, helindone scarlet S, helindone fast scarlet R, thioindigo red B, thioindigo scarlet, vat red.
		H₂S is evolved Becomes yellow or colour- less Colour returns on exposure to air. Apply to Indigo class. Also heat fibre in dry tube :—**Sulphide dyestuff**	11	Thiogene rubine, &c.
	Decolourised and colour not restored by air or by persulphate :—Azo class. Boil with soap solution and white mercerised cotton	The colour is not stripped Cr in ash :—**Mordant Azo dyestuff** The white cotton is not stained. Boil with pyridine	10	Chrome red, brilliant chrome red, chrome bordeaux, &c.
		The colour is stripped —**Insoluble Azo colour** The white cotton is stained Salt dye- stuff Test ash for Cr and Cu	9	Paranitraniline red, alphanaphthylamine bordeaux, chloranisidine pink, nitroanisidine pink, scarlet and reds from naphthol AC.
		Cr or Cu present :—**Azo Salt dye- stuff after- treated**	8	Diamine fast red F, &c.
		No Cr or Cu present .—**Azo Salt dyestuff**	7	Benzopurpurine, diamine scarlets, diamine reds, benzo fast scarlets, diazo brilliant scarlet, rosanthrenes, Zambesi red, erica, diamine rose, geranine, rosophenine, &c.
	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution :—**Basic dyestuff** (on tannin or other mordant). Transfer to wool and boil with hydrosulphite AX	Wool decolourised Colour not restored by air or by persul- phate :—**Azo class**	6	Janus red.
		Wool decolourised. Colour does not re- turn on exposure to air, but is restored by persulphate :—**Triphenyl- methane class**	5	Magenta, fuchsine, new fuchsine, isorubine, cerise, grenadine, &c.
		Wool decolourised. Colour returns on exposure to air :—**Azine class**	4	Safranines, rhoduline reds and pink, azine scarlet, induline scarlet, neutral red, &c.
		Wool not decolourised :—**Pyrone class**	3	Rhodamines, rhodines, irisamine, anisoline, rosazein, rhoduline pink, acridine reds, &c.
	The colour is stripped :—Acid dyestuff. Trans- fer to wool and boil with hydro- sulphite AX	Decolourised. Colour not restored by air or persul- phate :—**Azo class**	2	Crocein scarlets, brilliant croceines, Palatine scarlet, fast reds, &c.
		Not decolourised :—**Pyrone class**	1	Eosines, phloxine, erythrosine, rose bengal, &c.

RECOGNITION OF DYES ON VEGETABLE FIBRES.

TABLE X.—PURPLE AND VIOLET COLOURS. (1 : 100)

Boil for a quarter of a minute with saline caustic soda, rinse with cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).

Boil with weak ammonia (1 : 100)

The colour is not stripped.

Coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with hydrosulphite BX

Decolourised or yellowish. Colour restored on exposure to air :—Azine, Oxazine, Thiazine, or Indigoid classes. Apply lead acetate test. Also heat fibre in dry test-tube

Condition	No.	Dyestuff
No H₂S is evolved :—Anthracene Vat dyestuff	20	Indanthrene violet or violanthrene.
H₂S is evolved :—Sulphide dyestuff	19	Thiogene dark red, &c.

The colour is unaffected or only changed in shade, being restored to original on exposure to air :—Pyrone or Anthracene class. Test ash for mordant

Al or Cr is present :— Mordant dyestuff		
The colour on reduction is browner or darker	18	Alizarin cyanine 3R, alizarin bordeaux.
The colour on reduction is unchanged	17	Gallein, alizarin violet, alizarin claret, alizarin cyclamine, alizarin red on Cr mordant.

Mordants are absent. Apply lead acetate test

Cr is absent. Coloured vapours on heating :—Indigoid dyestuff	16	Ciba violet, ciba heliotrope, thioindigo violet, helindone violet.
Cr is present. No coloured vapours on heating :—Mordant Oxazine dyestuff (not falling in group 7)	15	Gallocyanine, modern violet, ultra violet, coreine, &c.

No H₂S is evolved. Test ash for mordant

H₂S is evolved :—Sulphide dyestuff	14	Thiogene violet, katigene violet, hydrone violet, &c.

The colour is not stripped Cr present in ash :—Mordant Azo dyestuff	13	Chrome bordeaux, chrome prune, &c.
The colour is stripped with pyridine. Insoluble Azo colour	12	Benzidine puce.
Colour destroyed, giving yellow solution. Fe present in ash :—Alizarin red on Fe mordant	11	Alizarin purple.

The white cotton is not stained. Boil with hydrochloric acid (1 : 20)

Cr or Cu present :—Azo Salt dyestuff after-treated	10	The undermentioned (col. 9) coppered or chromed.
No Cr or Cu present :—Azo Salt dyestuff	9	Violets of the diamine, benzo, Congo, Hessian, Columbia, chlorazol, chlorantine, dianil, oxamine, and rosanthrene series.

The white cotton is stained. Boil with soap solution and white mercerised cotton

Iron (decolourised slowly). Boil with soap solution and white mercerised cotton

Decolourised and colour not restored by air or persulphate :—Azo class or Alizarin on Iron (decolourised slowly).

The white cotton is not stained. Boil with hydrochloric acid (1 : 20)

The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin

Not precipitated :—Basic dyestuff. Transfer to wool and boil with hydrosulphite AX

Precipitated.— Cr present in ash :—Basic Mordant dyestuff. Boil cotton with hydrosulphite BX		
Decolourised only slowly. Colour does not return in air, but is restored by persulphate :—Triphenylmethane class	8	Chrome violet.
Decolourised. Colour returns on exposure to air :—Oxazine class	7	Gallocyanine, modern violet, ultra violet, coreine, prune, &c.

The colour is stripped :—Basic dyestuff (on tannin or other mordant). Add chromium fluoride reagent to the extract

Decolourised. Colour is not restored by air or persulphate :—Azo class	6	Janus claret red, &c.
Decolourised. Colour does not return in air, but is restored by persulphate :—Triphenylmethane class	5	Methyl violets, ethyl violet, benzyl violet, crystal violet, &c.
Decolourised. Colour returns on exposure to air :—Azine (Oxazine or Thiazine) class	4	Methylene violet, rhoduline violet, iris violet, neutral violet, tannin heliotrope, &c.
Not decolourised :—Pyrone class	3	Anisoline.

The colour is stripped.—Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate :—Triphenylmethane class

The ammoniacal solution is violet	2	Acid violets, formyl violets, alkali violet, guinea violet, &c.
The ammoniacal solution is colourless, but becomes blue on acidifying	1	Red shades of soluble and alkali blues.

RECOGNITION OF DYES ON VEGETABLE FIBRES

TABLE XL.—BLUE COLOURS.

Boil with weak ammonia (1 : 100)

The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).

Branching tests	Final condition	No.	Dye identified
Colour unaffected or becomes darker, browner, &c., the original colour being restored on exposure to air :—Anthracene mordant or anthracene vat dyestuff (also Ultramarine). Boil with 90 p.c. formic acid. Reduce original fibre with hydrosulphite BX — **The colour is not much affected. Test ash for Cr**	Cr absent :— **Anthracene vat dyestuff**	18	Indanthrene blues, algole blues.
—	Cr present in ash :—**Alizarin dyestuff** on Cr	17	Alizarin blue, alizarin cyanines or anthracene blues on Cr mordant.
The colour is stripped. Al in ash. Apply lead acetate test	No H₂S evolved :— **Alizarin dyestuff** on Al	16	Alizarin cyanines or anthracene blues on Al mordant, erganone blues.
—	H₂S is evolved	15	Ultramarine.
A coloured acid extract precipitate by tannin is not obtained. — Decolourised or yellowish. Colour is restored on exposure to air :—Azine, Oxazine, Thiazine, or Indigo class. Apply lead acetate test	Colour changed to greenish-yellow, which can be diazotised and developed with betanaphthol :— **Primuline azo colour**	14	Primuline developed with naphthylamine ether.
No H₂S evolved. Heat fibre carefully in dry test-tube	No coloured vapour. Cr in ash :—**Mordant thiazine or oxazine** (not falling in group 6)	13	Brilliant alizarin blue, gallocyanine, gallamine blue, prune, celestine blue, delphine blue, &c.
—	Violet vapours evolved :—**Indigoid dyestuff**	12	Indigo (natural and synthetic), indigo MLB 2B, 4B, 5B, 6B, and T, ciba blue, bromindigo FB.
—	H₂S is evolved :— **Sulphide dyestuff**	11	Blues of the immedial, katigene, thiogene, pyrogene, sulphur, &c., series, hydrone blues.
Decolourised and colour not restored by air or persulphate.—Azo class. Boil with soap solution and white mercerised cotton — **The white cotton is not stained.**	Colour is stripped by boiling pyridine :— **Insoluble azo colour**	10	Dianisidine blue, blue from naphthol AC.
The white cotton is stained :—Salt dyestuff. Test ash for Cr and Cu	Cr or Cu present :— **Azo salt dyestuff** after-treated	9	The undermentioned (col. 8) coppered or chromed.
—	No Cr or Cu present :—**Azo salt dyestuff**	8	Blues of the diamine, benzo, Congo, Columbia, chlorazol, dianil, oxamine, Chicago, &c., series.
The colour is completely or largely stripped. A coloured acid extract, which is precipitated by tannin :—Basic dyestuff (on tannin or other mordant) or Basic mordant dyestuff. Add chromium fluoride reagent to the extract. — **Precipitated. Cr present in ash :—Basic mordant dyestuff. Boil cotton with hydrosulphite BX**	Decolourised slowly. Colour restored only by persulphate :— **Triphenylmethane class**	7	Chrome blue.
—	Decolourised. Colour returns on exposure to air :— **Oxazine class**	6	Gallocyanine, gallamine blue, celestine blue, prune, coreine, ultracyanine, modern cyanine, &c.
Not precipitated.—Basic dyestuff. Transfer to wool and boil with hydrosulphite AX	Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—**Triphenylmethane class**	5	Victoria blue, night blue, turquoise blue, setocyanine, &c.
—	Colour changes to red just before being decolourised. Colour returns violet or blue : **Safranine azo dyestuff**	4	Indoine blue, Janus blue, naphthindone blue, diazine blue, &c.
—	Decolourised. Colour returns on exposure to air :—**Azine, Oxazine, or Thiazine class**	3	Methylene blue, Nile blue, Capri blue, indazine, Basle blue, Moldola's blue, fast blue, cresyl blue, rhoduline blue, nitroso blue, &c.
The colour is stripped :—Acid dyestuff (or Prussian blue)	The extract is colourless and remains so on acidification. FeCl₃ gives a blue precipitate	2	Prussian blue.
—	The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolourised by hydrosulphite A, and restored by persulphate :— *Triphenylmethane class	1	Alkali blues, soluble blues, chlorazol brilliant blue, isamine blue, betamine blue, brilliant dianil blue, brilliant sky blue.

RECOGNITION OF DYES ON VEGETABLE FIBRES.

TABLE XII.—GREEN COLOURS.

Boil with weak ammonia (1 : 100)

The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid. A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with hydrosulphite BX.

Condition	No.	Dyestuff
Reduced to yellow. Restored by air oxidation :—**Indigoid dyestuff**	20	Ciba green, helindone green.
Reduced colour is blue. Green shade restored by air	19	Algole green.
Reduced colour is dark maroon. Green shade restored by air	18	Indanthrene green or viridanthrene, leucole dark green B.
Reduced colour is brownish-olive. H₂S evolved on applying lead acetate test	17	Indanthrene olive or olivanthrene.
Colour of fibre rather paler, solution brownish-yellow	16	Cœruleine, anthracene green.
Colour of fibre becomes grey, solution red. Ni in ash	15	Alizarin green S on Ni-Mg mordant.
Colour unaffected. Solution colourless. Cr in ash	14	Alizarin green S on Cr mordant.
Reduced colour is brownish-red. Green restored by persulphate, but not by air. Boiling HCl (1 : 20) gives bright green solution	13	Alizarin viridine, brilliant alizarin viridine, alizarin cyanine green.
No H₂S is evolved :—**Mordant Oxazine (or Thiazine)**	12	Gallanilic green, indalizarine, &c.
H₂S is evolved :—**Sulphide dyestuff**	11	Greens of the immedial, katigene, thiogene, pyrogene, cross-dye, sulphur, and thionol series.
The colour is changed to greenish yellow, not restored to green by air, which can be diazotised and developed red with betanaphthol :—**Primuline Azo class**	10	Primuline developed with amidodiphenylamine.
Not decolourised. Cr is present in the ash :—**Mordant Azo dyestuff**	9	Diamond green, &c.
Colour destroyed. Fe is present in the ash :—**Nitroso class**	8	Russian green, fast green O, steam green, Alsace green, gambines, dioxine, &c.
Cr or Cu present :—**Azo Salt dyestuff after-treated**	7	The undermentioned (col. 6) coppered or chromed.
Cr and Cu absent :—**Azo Salt dyestuff**	6	Diamine green, benzo green, Columbia green, chloramine green, &c.
Precipitated. Cr in ash. Fibre decolourised by hydrosulphite BX, the colour not returning in air, but restored by persulphate :—**Triphenylmethane class**	5	Chrome green.
Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—**Triphenylmethane class**	4	Brilliant green, malachite green, methyl green, Victoria green, setoglaucine, new fast green, &c.
Colour becomes red just before being decolourised. Colour returns violet or green on exposure to air :—**Safranine Azo class**	3	Janus green, diazine green, &c.
Decolourised. Colour returns on exposure to air :—**Azine, Oxazine, or Thiazine class**	2	Fast green M, methylene green, azine green, Capri green, &c.
The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate :—**Triphenylmethane class**	—	Acid greens, guinea green, Neptune green, naphthalene green, agalme, green.

Intermediate column headings:

- No Cr or Ni present in ash :—**Anthracene Vat dyestuff**
- The ash contains Cr or Ni :—**Anthracene Mordant dyestuff**
- Reduced colour is brown. Green shade returns on exposure to air. Boil with hydrochloric acid (1 : 20)
- Decolourised. Colour returns on exposure to air.—**Azine, Oxazine, or Thiazine class**
- The white cotton is not stained. Boil with hydrochloric acid (1 : 20)
- Decolourised and colour not restored by air.—**Azo or Nitroso class**. Boil with soap solution and white mercerised cotton
- The white cotton is stained.—**Salt dyestuff.** Test ash for Cr and Cu

Left (vertical) headings:

The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution :—**Basic dyestuff** (or tannin or other mordant) or **Basic Mordant dyestuff**. Add chromium fluoride to the extract.

Not precipitated :—**Basic dye-stuff.** Transfer to wool and boil with hydrosulphite AX

The colour is stripped :—Acid dyestuff.

RECOGNITION OF DYES ON VEGETABLE FIBRES

TABLE XIII.—BROWN COLOURS.

	Result
Cr and Cu absent :—Anthracene vat dyestuff, &c.	**15** Indanthrene maroon, algole brown, leucole browns, cibanone brown, paramine brown (p-phenylene diamine oxidised on fibre).
No H₂S is evolved. Test ash for Cr and Cu — Mordant dyestuff. Boil with HCl (1 : 20). Solution brown, fibre unaffected	**14** Cutch.
Not stripped or only slightly. Boil with dilute caustic soda (10 p.c.). Fibre and solution dull violet	**13** Alizarin orange on Cr mordant, alizarin red or purpurin on Cr.
Completely stripped	**12** Anthragallol, anthracene brown, alizarine brown.
H₂S is evolved :—Sulphide dyestuff	**11** Immedial cutch, cross-dye brown, katigene browns, pyrogene browns, thiogene browns, &c.
Decolourised and original colour restored by air :—Indigoid class	**10** Helindone brown G, ciba brown, thioindigo brown.
The shade is changed to greenish yellow, which can be diazotised and developed red with beta-naphthol :—Primuline azo-colour	**9** Primuline developed with metaphenylene diamine, terra-cotta, &c.
The colour is not stripped :—Mineral colour. Treat with sodium bisulphite in the cold. Not decolourised	**8** Iron buff, khaki (oxides of Cr and Fe).
Decolourised	**7** Manganese bronze.
The colour is stripped—Insoluble azo-colour. Test ash for Cu. Cu present	**6** Paranitraniline cutch (para red coppered).
Cu absent	**5** Para brown (chrysoidine and paranitraniline), benzidine or toluidine brown.
The white cotton is stained :—Salt dyestuff. Test ash for Cr and Cu. Cr or Cu present :—Azo salt dyestuff after-treated	**4** The undermentioned (col. 3) coppered or chromed.
Cr and Cu absent :—Azo salt dyestuff	**3** Browns of the diamine, benzo, Congo, dianil, chlorazol, Columbia, Hessian, oxamine, and toluylene series.
The colour is stripped, giving acid extract which is precipitated by tannin solution :—Basic dyestuff. The dyestuff transferred to wool is permanently decolourised by hydrosulphite AX :—Azo class	**2** Bismarck brown, Janus brown, tannin brown, &c.
The colour is stripped :—Acid dyestuff. Transferred to wool it is permanently decolourised by hydrosulphite AX :—Azo class	**1** Fast brown, naphthylamine brown, acid brown, &c.

Column headings (left to right):

The colour is not stripped. Boil with weak ammonia (1 : 100)

Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid (1 : 100)

A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with hydrosulphite BX

Decolourised and colour not restored on exposure to air or by per-sulphate :—Azo class and Mineral colours. Boil with soap solution and white mercerised cotton

The white cotton is not stained. Boil with pyridine

Unaltered or changed in shade, becoming darker, paler, yellower, &c. Apply lead acetate test

Cr or Cu (or both) present :—Mordant dyestuff. Boil with HCl (1 : 20)

RECOGNITION OF DYES ON VEGETABLE FIBRES

TABLE XIV.—BLACK AND GREY COLOURS.

Boil with weak ammonia (1 : 100)

The colour is not stripped. — Boil with dilute hydrochloric acid (1 : 5)

Boil for one minute with saline caustic soda, rinse, and boil with water and dilute hydrochloric acid (1 : 20)

The colour is not stripped (or only slightly). — A coloured acid extract precipitable by tannin is not obtained. — Reduce original fibre with hydrosulphite BX. The colour is unaffected or changed in shade (becoming brown, maroon, &c.)

No.	Test / class	Dye
15	Colour not changed by reduction (or very slightly) :—**Anthracene class.** Test ash for Cr. — Cr absent :—**Anthracene vat dyestuff**	Indanthrene grey, indanthrene black, cibanone black, helindone black.
14	Cr present :—**Anthracene mordant dyestuff**	Alizarin cyanine black, alizarin blue black B.
13	The reduced colour is brown. Only slowly and imperfectly restored to black by air, but at once by persulphate. Cr present in ash.—**Naphthalene mordant dyestuff**	Naphthazarine S, alizarin black S, alizarin blue black SW, naphthomelane.
12	The reduced colour is brown, but is rapidly restored to black on exposure to air.—**Azine, Oxazine, or Thiazine class.** Apply lead acetate test. — No H_2S is evolved. Fibre becomes reddish-brown on boiling with bleaching powder solution 5° Tw.—**An oxidation black**	Aged-aniline black, Prussiate black, one-bath aniline black, steam aniline black, diphenyl black.
11	H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution 5° Tw —**Sulphide dyestuff**	Blacks of the immedial, katigene, cross-dye, pyrogene, thiogene, thionol, pyrol, sulphur, &c., series.
10	Decoloured and colour restored by air. Gives violet vapours on heating in dry tube - **Indigoid dyestuff**	Ciba grey G and B.
9	The white cotton is not stained. Colour is stripped by boiling pyridine — **Insoluble azo colour**	Azophor black, &c.
8	Decolourised and colour not restored by air or persulphate — **Azo class.** Boil with soap solution and white mercerised cotton. The white cotton is stained. Test ash for Cr and Cu. — Cr or Cu present.— **Azo salt dyestuff after-treated**	The undermentioned (col. 7) coppered or chromed.
7	Cr and Cu absent :— **Azo salt dyestuff**	Blacks of the diamine, oxydiamine, benzo, Columbia, diamil, Pluto, &c., series. Also diaminogen, diazo blacks, &c. (developed or coupled).
6	The colour is largely stripped and the acid extract is precipitated by tannin solution :—**Basic dyestuff.** Transfer to wool and boil with hydrosulphite AX. Colour becomes red just before being decolourised Violet or violet-blue colour returns in air **Safranine azo class.**	Janus black, Janus grey, diazine grey.
5	Decolourised. Colour returns on exposure to air .— **Azine, Oxazine, or Thiazine class.**	Methylene grey, new methylene grey, new fast grey, nigrisine, &c.
4	**The colour is stripped** — Solution red. Cr in ash	Logwood black on chrome mordant, noir reduit
3	Solution orange. Fe in ash	Logwood black on iron mordant.
2	Fibre and solution colourless	Tannate of iron.
1	The colour is stripped :—**Acid dyestuff.** The dyestuff transferred to wool and boiled with hydrosulphite AX is permanently decolourised :—**Azo class.**	Naphthol blacks, naphthylamine blacks, Palatine black, &c.

edition of Vogel's 'Practische Spectralanalyse irdischer Stoffe' (1889), charts were given of the absorption bands of various dyestuff solutions. This work was greatly extended in 'Formánek's Spectralanalytischer Nachweis Künstlicher organischen Farbstoffe' (1900), which contains a systematic scheme for the spectroscopic identification of upward of 350 distinct dyestuffs. In a later publication (1905) entitled 'Qualitative Spectralanalyse anorganischen und organischen Körper,' Formánek has extended his data to include the natural colouring matters, and, in conjunction with E. Grandmougin, has republished his tables as 'Untersuchung und Nachweis organischen Farbstoffe auf spectroscopischen Wege.'

The value of spectroscopic tests for the identification of dyestuffs on the fibre is limited to those dyestuffs which can be removed without change by suitable solvents.

Spectroscopic examination of dyed fibres has not yielded useful results.　　W. M. G.

NOTE.—Green's scheme of identification of dyes and the annexed Tables are printed by permission of Prof. A. G. Green and Messrs. Chas. Griffin & Co., Ltd

DYER'S BROOM, *Genista tinctoria* (Linn.) (*Dyer's broom, Dyer's greenweed*; *Genêt, Genestrole, Trentanel*, Fr. ; *Ginster*, Ger) is found in the pastures, thickets, and waste places throughout Central and Southern Europe, across Russian Asia to the Baikal, and northward to Southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland. The fact that it contains a yellow colouring matter is recorded by numerous writers, and the following embody the principal references to the dyeing and general properties of the plant : Bancroft (Philosophy of Permanent Colours, 1813, 2, 108) ; Gmelin (Handbook of Chemistry, 16, 517) ; Berthollet (On Dyeing, 1824, 2, 242) ; Gonfreville (L'Art de la Teinture des Laines, 501) ; Leuchs (Farben u. Farbekunde, 1846, 2, 309), and Schutzenberger (Traité des Matières Colorantes, 1867, 4, 422).

To isolate the colouring matters, a hot aqueous extract of the plant is treated with lead acetate solution, and the pale yellow viscous precipitate is collected and decomposed by means of boiling dilute sulphuric acid. The clear liquid decanted from the lead sulphate deposits on cooling a dull yellow powder ; this is filtered off, dissolved in a little alcohol, and the solution poured into a large volume of ether, causing the separation of a dark-coloured resinous impurity. The clear liquid is evaporated, yielding a yellow crystalline residue, which consists of two substances. To separate these, advantage is taken of the fact that, with sulphuric acid in the presence of acetic acid, one only of these compounds gives an insoluble sulphate. This is collected and decomposed with water and the product crystallised from dilute alcohol. It is obtained as yellow needles, and was found to be identical with the *luteolin* of weld (*Reseda luteola*) (Perkin and Newbury, Chem. Soc. Trans. 1899, 75, 830).

Genistein $C_{14}H_{10}O_5$, the second colouring matter of dyer's broom, is present in the mother liquors obtained during the purification of the luteolin, and also in considerable quantity in the filtrate from the lead precipitate, from which

it is most readily isolated. To the boiling liquid ammonia is added, causing the separation of a lemon-yellow precipitate, which is collected and decomposed with boiling dilute sulphuric acid. The clear liquid is extracted with ether, and the extract evaporated, leaving a brownish crystalline mass. It is purified by crystallisation from acetic acid, and by conversion into the acetyl derivative.

Genistein crystallises in long colourless needles ; m.p. 291°–293° (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1312) ; soluble in alkalis with a pale yellow colouration. Alcoholic ferric chloride gives a dull-red violet colouration, and alcoholic basic lead acetate a lemon-yellow precipitate.

Triacetylgenistein $C_{14}H_7O_5(C_2H_3O)_3$, colourless needles, m.p. 197°–201° ; and *tetrabromgenistein* $C_{14}H_6Br_4O_5$, colourless needles, m.p. above 290°, have been described.

On digestion with boiling 50 p.c. potassium hydroxide, genistein gives *phloroglucinol* and *p-hydroxyphenylacetic acid.*

By methylation with methyl iodide in the usual manner, genistein dimethyl ether and methylgenistein dimethyl ether are produced.

Genistein dimethyl ether $C_{14}H_8O_3(OCH_3)_2$ forms colourless leaflets, melts at 137°–139°, and gives the *monacetyl* compound

$$C_{14}H_7O_3(C_2H_3O)(OCH_3)_2$$

minute colourless needles, m.p. 202°–204°. When decomposed with alcoholic potash, it forms *methoxyphenylacetic acid* and *phloroglucinol-monomethyl ether* (identified by means of its disazobenzene derivative).

Methylgenistein dimethyl ether

$$CH_3 \cdot C_{14}H_7O_3(OCH_3)_2$$

melts at 202° ; and the *acetyl* derivative

$$CH_3 \cdot C_{14}H_6O_3(C_2H_3O)(OCH_3)_2$$

forms colourless needles, m.p. 212°–214°. With alcoholic potash it gives *methoxyphenylacetic acid* and probably *methylphloroglucinol-monomethyl ether.*

Genistein diethyl ether $C_{14}H_8O_3(OC_2H_5)_2$ forms colourless needles, m.p. 132°–134° ; whereas *acetylgenistein diethyl ether*

$$C_{14}H_7O_3(C_2H_3O)(OC_2H_5)_2$$

melts at 168°–170°. Alcoholic potash gives p-*ethoxyphenylacetic acid.*

According to Perkin and Horsfall, genistein may be a *trihydroxyphenylketocumaran*:—
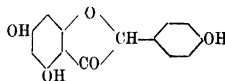
Genistein is a feeble colouring matter, and upon woollen cloth gives, with chromium mordant, a pale greenish-yellow ; with aluminium mordant, a very pale yellow ; and with iron mordant, a chocolate-brown shade.

Dyeing Properties of Dyer's Broom.—In this respect there is a close resemblance between dyer's broom and weld. The dyeing power of the former is distinctly the weaker of the two ; otherwise the only point of difference worthy of mention is that shown by the iron mordant, which, in the case of dyer's broom, gives a duller and more drab-coloured shade.

Luteolin is also present in the *Digitalis purpurea* (digito-flavone) (Fleischer and Fromm, Ber. 1899, 32, 1184; v. Kostanecki and Diller, *ibid.* 1901, 34, 3577), and in the flowers of *Antirrhinum majus* (Wheldale and Bassett, Bio-Chem. J. *l.c.*).
A. G. P.

DYMAL. Trade name for 'didymium' salicylate [Nd Pr]·[C₆H₄(OH)·CO₂]₇. A reddish-white substance, used as a dusting powder, having non-irritant and antiseptic properties.

DYNAMAGNITE, DYNAMITE v. EXPLOSIVES.

DYSANALYTE. A cubic or pseudo-cubic mineral consisting of titano-columbate of calcium with some ferrous oxide, cerium earths (up to 5 p.c.), and sodium. The amount of Cb₂O₅ given in various analyses ranges from nil to 26 p.c., and the mineral has sometimes been asserted to be identical with perofskite (CaTiO₃); the difficulties presented in the analysis of this mineral are, however, implied by its name, from δυσανάλυτος, 'hard to undo' It occurs as small black cubes in contact-metamorphic limestone at Sasbach in the Kaiserstuhl Mountains, Baden, and in metamorphic sandstone at Magnet Cove, Arkansas. L. J. S.

DYSCRASITE (antimonial silver). Antimonide of silver Ag₆Sb (Ag 84·3 p.c.) to Ag₃Sb (Ag 72·9 p.c.), occurring as silver-white masses with metallic lustre, but often with a dull yellowish or black tarnish. The material is sectile· H.=3½-4. Orthorhombic crystals, twinned to simulate hexagonal forms, are rare and not distinctly developed. According to T. Liebisch (1910), two compounds are represented, namely, cubic Ag₆Sb, with sp.gr. 10 05, and orthorhombic Ag₃Sb, with sp.gr. 9·63-9·82. The mineral is found in silver mines at Wolfach in Baden (where it is the chief ore), Andreasberg in the Harz, Allemont in France, and the Cobalt district in Ontario. L. J. S.

DYSODILE. A soft laminated carbonaceous substance of a yellowish-grey or green colour burning with a luminous flame, and a smell resembling that of burning caoutchouc. Found in Sicily and in Bavaria (Fricklinger, Jahrb. Min. 1875, 760; also Church, Chem. News, 34, 156; Potonié, Chem. Zentr. 1907, ii. 555).

DYSPROSIUM. Sym. Dy. At. wt. 162·5 (162·52 Kremers, Hopkins, and Engle, J. Amer.

Chem. Soc. 1918, 40, 598) (Urbain and Demenitroux, Compt. rend. 1906, 143, 598; Hinrichs, *ibid.* 1143). From erbia—one of the fractions obtained from ytterbite—Cleve separated an earth which he called 'holmia'; and from this material Lecoq de Boisbaudran isolated a simpler constituent, *dysprosia*, characterised by a well-marked absorption spectrum showing bands in the ultra-violet as well as in the visible region of the spectrum (Compt. rend. 1886, 102, 100). This oxide, one of the most basic constituents of holmia, was concentrated by precipitations with potassium sulphate and ammonia. Further fractionation of the nitrates and double nitrates gave a product rich in terbium and dysprosium (Urbain, Compt. rend. 1904, 139, 736; 1905, 141, 521). The latter is separated from terbium by fractional crystallisation of the ethyl sulphates, terbium and yttrium being concentrated in the least soluble fraction, whilst dysprosium accumulates in the middle fraction (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184; Compt. rend. 1906, 142, 785).

Dysprosium material of very high purity may be obtained by fractional crystallisation of the rare-earth bromates, followed by fractional crystallisation of the ethyl sulphates (Engle and Balke).

Dysprosium is separated from yttrium by crystallisation of the nitrate with the addition of bismuth nitrate.

Dysprosium forms a white *oxide* Dy₂O₃, but no peroxide. Its salts have a faint greenish-yellow tint: *chloride* DyCl₃,6H₂O; *nitrate* Dy(NO₃)₃,5H₂O, melting at 88° in its water of crystallisation, very similar to bismuth nitrate (Urbain and Jantsch, Compt. rend. 1908, 146, 127); *sulphate* Dy₂(SO₄)₃,8H₂O, brilliant yellowish crystals, stable at 110°, and completely dehydrated at 360°. For other salts, v. Jantsch and Ohl, Ber. 1911, 44, 1274.

Dysprosium stands first in the list of paramagnetic elements, its oxide Dy₂O₃ being 12·8 times more magnetic than ferric oxide. The high values for the magnetic susceptibility of the rare earths (yttria, erbia, &c.) fractionated by Cleve and Nilson are probably due to the presence of dysprosium (Urbain, Compt. rend. 1908, 146, 922). G. T. M.

E

EARTHNUT OIL v. ARACHIS OIL.

EAU DE COLOGNE v. PERFUMES.

EAU DE JAVELLE. Solution of sodium hypochlorite (v. *Bleach liquor*, art. CHLORINE).

EAU DE LUCE. *Aqua luciæ.* A milky liquid containing oil of amber, alcohol, and ammonia (v. AMBER, OIL OF).

EBONITE. *Sulphurised caoutchouc* (v. RUBBER).

EBULLIOSCOPE. An instrument for determining the strength of spirits of wine by means of its boiling-point.

ECBOLINE v. ERGOT.

ECGAINE. N-benzoylhydroxypropylnovec-

gonidene ester. A compound allied to cocaine and of the structure

$$CH_2 \cdot CH—CH \cdot CO_2Et$$
$$| \quad\quad |$$
$$NH \quad CH$$
$$| \quad\quad ||$$
$$CH_2 \cdot CH—CH$$
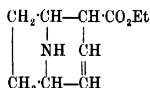
A crystalline base, more active than cocaine in its anæsthetic properties, is non-toxic and can be readily sterilised (Braun and Müller, Ber. 1918, 235; Chem. Werke Grenzbach, D. R. P. 301139).

ECGONINE v. COCAINE AND THE COCA ALKALOIDS.

ECHITAMINE, ECHITENINE *v.* DITA BARK.

ECHUJIIN *v.* DIGITALIS.

E. C. POWDER *v.* EXPLOSIVES.

EDESTIN. A crystalline proteid substance found in the seeds of hemp, sunflower, and castor-bean, capable of uniting with acids to form salts (Osborne, J. Amer. Chem. Soc. 24, 39).

EDIBLE OILS AND FATS. Under this term are comprised those oils and fats which serve as food. Most of the edible oils and fats, such as olive oil, cod liver oil, suet, lard, butter-fat, cacao butter, goose fat, &c , are immediately fit for consumption, if ' rendered ' with sufficient care. Hence they rarely need undergo a process of technical purification, except simple filtration, before they are placed on the market. This applies, however, only to the freshly (' first ') rendered products, as contact with putrescible organic matter rapidly causes hydrolysis of the oils and fats, so that, *e.g* , lard or olive oil which has been allowed to remain in contact for some little time with the organic tissues from which they have been derived, readily become rancid, and therefore unfit for food in their original state This applies with especial force to cod liver oil.

The large demand made on the market by the rapidly growing consumption of oils and fats has, however, led to the employment of second and even third ' renderings,' in the case of animal fats, and second or third ' expressions ' in the case of vegetable oils and fats. Such products contain, as a rule, notable amounts of free fatty acids, and small quantities of extractive substances, all of which must be removed before the oils and fats become suitable for food purposes. The processes applied to the purification and decolourisation are treated as deep secrets. It may, however, be stated that most of the processes are based on physical methods of refining (*see* OILS AND FATS).

Chemicals involving the use of mineral acids must be altogether excluded from the purview, of the refiner, since the mineral acids, however carefully they may be removed by subsequent washing, impart an objectionable flavour to the products, thus rendering them useless for edible purposes. Alkalis or alkaline earths are not so objectionable, and are, therefore, used commercially for the removal of free fatty acids. (A notable example of this kind is furnished by the usual method of refining cotton-seed oil.) The alkalis and alkaline salts chiefly employed in practice are caustic soda, sodium carbonate, sodium silicate, lime, and magnesia. Baryta has also been proposed (and patented), but its poisonous properties would prohibit its use.

Whereas all animal oils and fats, when freshly prepared, are suitable for food, this holds good only in a somewhat restricted sense of vegetable oils and fats. If the vegetable oils and fats are free from objectionable substances they may hold in solution or may have dissolved from the vegetable matter from which they have been obtained by expression or boiling out, they are suitable for edible purposes, and are so used to a very considerable extent.

We know, however, that a number of oils which contain non-fatty toxic or injurious substances, such as tung oil, calophyllum oil, curcas oil, croton oil In the case of castor oil, the fatty acids themselves are injurious to health ; hence

castor oil is unusable as a foodstuff. Experience has also shown that the fats belonging to the Chaulmoogra group are injurious to health. All these oils must, therefore, be excluded from the list of edible oils.

Oils which are regarded as palatable in one part of the world are not used as food in other parts. Thus, whereas rape oil and linseed oil find a ready market for edible purposes in India, these oils are at present used in exceptional cases only as table oils in Western Europe. They are replaced in richer countries by cotton-seed oil, sesamé oil, arachis oil, poppy-seed oil, and olive oil. The increased consumption of the available edible oils and fats has created, during the last decades, a new and growing industry.

Amongst the most important developments in this industry is the preparation of coco-nut oil and palm-kernel oils for edible purposes (*see* COCO-NUT OIL and PALM-KERNEL OIL). Mixtures of several edible oils are now largely prepared as ' table oils ' to replace olive oil. Amongst these substitutes the most important are : arachis oil, sesamé oil, cotton-seed oil, and to some extent also soya-bean oil. Mixtures of edible vegetable and animal oils and fats are chiefly represented by the ' suet substitutes,' which are prepared by mixing tallow with cotton-seed oil, and by ' lard substitutes,' which represent a mixture of animal fats with cotton-seed oil, maize oil, &c. Until a few years ago, ' compound lard ' contained frequently no lard whatever, but, according to legislation in the United States, ' lard compounds ' or ' lard substitutes ' must now contain at least 50 p.c. of lard (*see* LARD SUBSTITUTES).

Another development of the industry has been the introduction of hardened or hydrogenated oils, which are now extensively used as constituents of margarine (*see* HYDROGENATED OILS).

The manufacture and sale of edible oils and fats has assumed such considerable importance that legislation has stepped in to protect the public against fraudulent practices both as regards the commercial description of a ' blended ' fat and the absence of injurious substances (*see* MARGARINE).

The changes in the character of fats during cooking have been described by Masters and Smith (Analyst, 1914, 39, 347).   J. L.

EDINOL. Trade name for *p*-amino-saligenin hydrochloride. Used as a photographic developer.

EDULCORATION. The act of washing insoluble matter so as to remove any soluble impurity.

EFFLORESCENCE. This term is applied to two or three different phenomena, characterised by the formation of a loose pulverulent deposit on the surface of a solid body.

1. Crystallised salts are said to effloresce when they lose their water of crystallisation and fall to powder, *e.g.* normal sodium carbonate.

2. The formation of a pulverulent crystalline deposit on the surface of a porous body, in consequence of the crystallisation of a salt existing in solution within its pores, or formed from materials existing therein, is also called efflorescence ; *e.g.* the crystallisation of potassium nitrate on the surface of the earth or in caves, as

in India, or on saltpetre plantations ; of sodium sulphate and carbonate on walls ; of alum on alum-slate ; of ferrous sulphate on iron pyrites, &c. In all these cases the solution of the salt is drawn by capillary action to the surface of the solid body, and there crystallises in consequence of the evaporation of the water.

3. The term ' efflorescence ' is likewise applied to the effect which sometimes takes place when a saline solution is left to evaporate slowly in an open vessel. The solid salt separates in dendritic crystals just where the surface of the liquid touches the side of the vessel, and the solution, rising by capillarity between these crystals, forms a fresh crystallisation just above the first layer ; and this process is continually repeated till the crystallisation thus formed extends over the edge of the vessel, and sometimes down to the table on which it stands. Sal-ammoniac and other ammonia salts often effloresce in this manner. The effect may be prevented to a certain extent by greasing the edge of the vessel, or better, by quickly boiling the solution, or evaporating it by heat from above.

EGG. The egg of the common fowl, *Gallus Bankiva*, consists of four principal parts : the *shell* ; the *white* ; the *yolk* or *vitellum* ; the *white yolk* or *germinal cell* ; and the membranes separating these parts. The usual weight of an egg is 40–60 grams ; of this the shell and shell membrane form 5–8 grams ; the yolk, 12–18 grams ; and the white, 23–34 grams.

The shell has the composition :

Calcium carbonate	. . .	89·6 p.c.
Phosphates of lime and magnesia		5·7 „
Organic matter and sulphur	.	4 7 „

The colouring matter of egg-shells is a bile pigment (Liebermann, Ber. 11, 606).

The *shell membrane* or *membrana putaminis* separating the white from the shell is double, the two parts being in contact over the greater part of the inner surface of the shell, but separated by an air-space at the broad end of the egg. These membranes are composed of a proteid substance allied to keratin (Liebermann). Abderhalden and Strauss have examined the products of hydrolysis of *ovokeratin*, and find them to be, from 100 grams of substance : 3·9 grams glycine ; 3·5 grams alanine ; 1·1 gram amino-valeric acid ; 7·4 grams leucine ; 4·0 grams proline ; 8·1 grams glutamic acid ; and 1·1 gram aspartic acid (Zeitsch. physiol. Chem. 1906, 48, 530).

The white is a faintly yellow albuminous fluid enclosed in large cells of thin membrane. The fluid has sp.gr. 1·045, and is really mobile, though it appears viscous because of its confinement by the cell walls. It has an alkaline reaction. Kojo (Zeitsch. physiol. Chem. 1911, 75, 1) gives the following analysis :

Water	.	.	.	.	87·71 p.c.
Ash	.	.	.	.	0·4 „
Organic solids	.	.	.	11·89 „
Total nitrogen	.	.	.	1·75 „
Dextrose	.	.	.	.	0·55 „

The organic solids consist mainly of proteins, a small amount of dextrose, and traces of fats, lecithin, and cholesterol. Salkowski showed that glucosamine was also present (Biochem. Zeitsch. 1911, 32, 335).

The protein substances of egg white are all gluco-proteids, and in their solution and precipitation properties are similar to globulins, albumins, or proteoses (*v.* art. PROTEINS).

Ovoglobulin separates from egg white partly on dilution with water, and completely if the solution be saturated with magnesium sulphate or ammonium sulphate. By repeated solution in water and reprecipitation, part becomes insoluble (Langstein, Hofmeister's Beitrage, 1), and it is probably a mixture of several globulins (Corin and Berard, Bull. Acad. Belg. [3] 15, 643). The globulins form about 6·7 p.c. of the total proteids of egg white (Dillner, Hammarstein's Text-book Physiol. Chem. 430).

Ovalbumin is the chief proteid constituent of egg-white. It is obtained crystalline by precipitating the globulins with ammonium sulphate, as above, and allowing the filtrate to evaporate. (For details of methods, *see* Hofmeister, Zeitsch. physiol. Chem. 16, 187 ; Osborne and Campbell, J. Amer. Chem. Soc. 1900, 22, 422 ; Rosenkrantz, J. Russ. Phys. Chem. Soc. 1906, 38, 2 ; and Mayer, Compt. rend. 1906, 143, 515.)

Pure ovalbumin crystallises in large, well-formed needles. A 2·5 p.c. solution in water becomes turbid at 60°, and at 64° yields a flocculent coagulum The addition of sodium chloride to the solution raises the temperature of coagulation (Osborne and Campbell, *l.c.* ; Starke, Pflüger's Archiv. 12, 18).

The composition of ovalbumin is :

C	H	N	S	P	O
52·75	7·10	15·51	1·62	0 12	22·90 p.c.

(Osborne and Campbell, *l.c.* 441 ; in agreement with Hopkins, J. Physiol. 25, 306 ; and Hammarsten, Zeitsch. physiol. Chem. 9, 304).

Many attempts have been made to assign a formula to ovalbumin. Latham (Biochem. J. 1908, 3, 207 *et seq*) gives it a molecular weight of 5473, and the formula $C_{240}H_{397}N_{65}O_{75}S_3$, but this must be regarded as an approximation only.

It has been characterised by determining the various amino-acids yielded on hydrolysis with hydrochloric acid of sp.gr. 1·19 (*v.* art. PROTEINS). 100 grams ovalbumin yield : alanine, 2·1 grams ; leucine, 20·0 grams ; phenyl-alanine, 4·4 grams ; tyrosine, 1·1 gram ; cystine, 0·3 gram ; proline, 2·3 grams ; aspartic acid, 1·5 grams ; and glutamic acid, 8·0 grams (Abderhalden and Pregl, Zeitsch. physiol. Chem. 1905, 46, 24 ; Osborne, Jones, and Leavenworth, Amer. J. Physiol. 1909, 24, 252 ; Levene and Beatty, Biochem. Zeitsch. 1907, 4, 305).

The specific rotation of pure albumin is given as −31° (Willcock, J. Physiol. 1908, 37, 27), −30·70° (Hopkins, ibid. 25, 306), and −29·31° (Osborne and Campbell, *l.c.*).

The precipitation of albumin by acids and salts is a completely reversible reaction (Galeotti, Zeitsch. physiol. Chem. 1905, 44, 461), and follows the law of mass action (Ostwald, Chem. Soc. Abstr. 1908, i. 375 ; Gerrini, Zeitsch. physiol. Chem. 1906, 47, 287).

Conalbumin. Only about one-half of the proteid of egg white can be obtained as crystallised ovalbumin ; the other fractions have a higher rotation and sulphur content. By heating these fractions at 65°, *conalbumin is*

obtained as a coagulum, which, when dried at 110°, has the following composition :—

C	H	N	S	O
52·25	6·99	16·11	1·70	22·95 p.c.

Its specific rotation is about −36° (Osborne and Campbell, *l.c.*; Panormoff, Chem. Zentr. 1898, 11, 487).

Ovomucoid is found in the residue after all proteids coagulated by heat have been removed from egg white (Neumeister, Zeitsch. Biol. 1890, 27, 369; Mörner, Zeitsch physiol. Chem. 1893, 18, 525). It forms about 10 p.c. of the proteids of egg white. It is not precipitated from solution by mineral acids or organic acids (except phosphotungstic and tannic acids) or by metallic salts.

The *inorganic constituents* of egg-white in 1000 parts are : Potash, 276–285 parts ; soda, 235–239 parts ; lime, 18–29 parts ; magnesia, 16–32 parts ; iron oxide, 4·4–5·5 parts ; chlorine, 238–205 parts ; phosphoric acid, 32–48 parts ; sulphuric acid, 13–26 parts ; silica, 3–20 parts ; carbon dioxide, 97–116 parts (Poleck and Weber, Hammarsten's Physiol. Chem. 1904, 432). Traces of fluorine have also been found (Nicklés, Compt rend 43, 885).

The yolk or yellow is contained within a membrane composed of a proteid allied to keratin (Liebermann, Pflüger's Archiv. 43). It is a viscous, opaque, yellow, alkaline emulsion having a mild taste, and consists chiefly of water, fats, and colouring matter, together with vitellin, lecithin, cholesterol, &c. Müller and Masuyama (Zeitsch. f. Biol. 1900, 39, 542) have found a diastatic enzyme in the yolk ; the presence of purine bases has been detected by Mesernitzki (Biochem. Zentr. 1, 739) ; and of creatinin by Salkowski (*l.c.*).

1000 parts of the yolk contain approximately : water, 480 parts ; fats, 228·4 parts ; proteid (vitellin), 156·3 parts ; lecithin, 107·2 parts ; cholesterol, 17·5 parts ; insoluble salts, 6·12 parts ; soluble salts, 3·53 parts.

According to Poleck, the ash of yolk of eggs contains, in 1000 parts : soda, 51·2–65·7 parts ; potash, 80·5–89·3 parts ; lime, 122·1–132·1 parts ; magnesia, 20·7–21·1 parts ; iron oxide, 11·9–14·5 parts ; phosphoric acid, 638·1–667·0 parts ; silicic acid, 5·5–14·0 parts.

The *fat* forms about 30 p.c. of the yolk, and may be extracted with ether. It is a mixture of solid and liquid fat, and contains 0·6 p.c. phosphorus, equivalent to 15·04 p.c. lecithin ; 61·5 p.c. of neutral fat ; and 23·2 p.c. free acids. The neutral fat contains glycerol and acid in such proportions as prove it to consist of *triglycerides* only (Thorpe, Arch. Nedér. Sci. Exact. Nat. 1901, 6, 155). On saponification it yields 40 p.c. oleic acid ; 38·04 p.c. palmitic acid ; and 15·21 p.c. stearic acid (Paladino, Biochem. Zeitsch. 1909, 17, 356).

Barbieri, by extracting yolks with carbon disulphide, obtained tristearin and triolein (Compt. rend. 1907, 145, 133), besides. cholesterol ; while MacLean has isolated pure tripalmitin from egg-fat (Biochem. J. 1909, 4, 168).

Lecithin (*v.* LECITHIN) is present both free and in combination with protein (Hanasse, Biochem. Ze'tsch. 1906, 1, 246). Commercial lecithins are usually prepared from eggs, and show a high choline content. Trier identified

β-aminoethyl alcohol in egg lecithin, isolating it as its gold chloride compound (Zeitsch. physiol. Chem. 76, 496). Lecithin is best prepared from dried egg yolks by Bergell's method (Ber. 1900, 2584). The extract prepared by boiling with 96 p.c. alcohol for 6 hours, is cooled to 0° and precipitated with an alcoholic · solution of cadmium chloride. The precipitate is filtered off, washed with 96 p.c. alcohol, dried in air, and extracted with ether. The residue is boiled with eight times its volume of 80 p.c. alcohol, and a concentrated solution of ammonium carbonate is added until the solution is free from cadmium. The filtered solution is cooled to −10°, and the precipitate is dissolved in chloroform, precipitated with acetone, and dried in *vacuò* over sulphuric acid.

After hydrogenation of egg lecithin, Paal and Oehme isolated stearic and palmitic acids, and suggest that linolic and palmitic acids are originally present (Ber. 1913, 1297).

Barbieri (Gazz. chim. ital. 1917, [1],1) stands alone among a host of investigators in his failure to isolate lecithin from egg yolk. He affirms that the phosphorus of egg yolk is present as inorganic phosphates, that the choline exists only as a degradation product of ovochromin, and that glycerol and fatty acids exist as constituents of fat, and not combined as lecithin.

Cholesterol is present in the yolk to the extent of about 1 p.c. (Juckenack, Zeitsch. Nahr. Genussm. 1899, 1905 ; Benecke, Bied. Zentr. 1881, 568). According to Serano and Palozzi (Chem. Zentr. 1911, ii. 772), it occurs as its oleic and palmitic esters.

Lutein, the colouring matter, was described by Maly (Chem. Zentr. 1881, 485) as a mixture of two substances : vitello-lutein, which is yellow and soluble in petroleum ; and vitello-rubrin, a red body soluble in carbon disulphide. The mixture is an orange-red amorphous substance, which is not affected by alkalis, and can therefore be isolated by hydrolysing the fats. C. A. Schunk (Proc. Roy. Soc. 1904, 170), as the result of spectroscopic examination, identified the yellow pigment of the hen's yolk with the L. xanthophyll, which he has isolated from grass. The characteristic spectroscopic behaviour of the lutein has been suggested as a test of the purity of commercial dried egg yolk (Lewin, Miethe, and Stenger, Pflüger's Archiv. 1908, 585). Willstätter and Escher (Zeitsch. physiol. Chem. 76, 214) isolated the pigment from the yolks of 6000 eggs, and obtained it in crystalline form, and showed it belonged to the xanthophyll group of pigments ; they showed also that a carotin-like pigment was present. Palmer (J. Biol. Chem. 23, 261) showed that the pigments of egg yolk were increased by feeding with rations rich in xanthophyll, yellow corn being particularly suitable for this purpose as a winter ration. The point is of importance to the poultry trade, since eggs with highly-coloured yolks are in great request.

Vitellin, the protein constituent of the yolk, is separated by mixing the yolks with brine, in which the protein is soluble, and extracting the fat, &c., with ether. It has the properties of a globulin, and, on dialysis or dilution of the solution, is precipitated. as a white granular substance. A solution coagulates at 70°–75°.

Vitellin thus obtained is a mixture of compounds of protein matter with lecithin, containing from 15–30 p.c. of the latter, called *lecithin-nucleovitellins*. The lecithin thus combined is not removed by ether, but is completely removed by alcohol, leaving an insoluble proteid, *nucleovitellin*, of constant composition, which, on digesting with pepsin, yields paranuclein.

It is probable that all these proteins are compounds of vitellin with phosphoric acid H_3PO_4, or some very simple organo-phosphoric acid. The composition of vitellin, free from phosphoric acid, is :

C	H	N	S	O
52·71	7·46	16·64	1·05	22·14 p c.

(Osborne and Campbell, J. Amer. Chem. Soc. 1900, 22, 413).

Plimmer states that another distinct protein 'livetin,' can be obtained from the yolk (Chem. Soc. Trans. 1908, 1500).

Berthelot and André determined the heat of combustion of egg yolk to be 8124 calories per gram (Compt. rend. 110, 925).

The germinal vesicle, or **white yolk,** forms a layer between the yolk and the yolk membrane, with a process extending to the centre of the yolk. It is enclosed in a membrane, and contains proteins, lecithin, and a nuclein rich in phosphorus (Meischer. Chem. Soc. Trans. 1871, 24, 746).

The space between the shell membranes at the broad end of the egg contains a mixture of oxygen, nitrogen, and carbon dioxide, richer in oxygen than the surrounding air (Hufner, Du Bois Reymond's Archiv. de Physiol. 1892, Phys. Abth. 54).

Eggs contain, on the average, about 4·6 mgms. of ferric oxide. This amount is increased by feeding the hens with foods rich in iron, and ' iron-eggs ' thus obtained have been recommended for therapeutic use, but are very costly (Hartung, Zeitsch. f. Biol. 1902, 43, 195 ; Hofmann, Zeitsch, anal. Chem. 1901, 40, 450).

Bertrand states that arsenic is normally present in the egg to the extent of $\frac{1}{500}$ mgm. (Compt. rend. 1903, 136, 1083), and that 1 mgm. boron occurs in 1 kgm. dried egg (Compt. rend. 1913, 156, 2027). •

Development.—During incubation the egg respires, giving off carbon dioxide and water, and absorbing oxygen. If this process be stopped by placing the egg in an inert gas, or by rendering the shell impervious to gases, the development of the chick ceases. The respiration is slight for the first four days of incubation, and then increases until, at the ninth day, the respiration of the egg is equal to that of a fowl, weight for weight. This respiration involves combustion of the fat of the egg, and a steady loss in weight (Pott, Landw. Versuchs. Stat. 23, 203 ; Chem. Soc. Abstr. 1879, 474).

Levene states that the quantity of xanthine bases and nuclein compounds increases with the growth of the embryo (Amer. J. Physiol. 1900, 3, xii.).

In egg-white the ratio albumin : ovomucoid of egg is constant during incubation (Bywaters and Roue, J. Physiol. 46, Proc. 33). After 3 days α-lactic acid was found (Anno, Zeitsch. physiol. Chem. 80, 237). In new-laid eggs the cholesterol is free, but gradual esterification

takes place, until at the time of hatching 40 p.c. is in ester form (J. Biol. Chem. 21, 23).

All the phosphorus in the chick is derived from the yolk and white, and, until the last few days of incubation, no lime is taken from the shell (Voit, Zeitsch. f. Biol. 13, 518 ; Pott, l.c.). At the end of incubation, the shell may supply some of the lime required (Carpiaux, Bull. Acad. Roy. Belg. 1908, 283 ; see also Plimmer and Scott, J. Physiol. 1909, 38, 247).

The freezing-point of fresh eggs is 0·427°–0·480°, and rises slightly as incubation proceeds, corresponding to a rise of osmotic pressure from 5·5 atmospheres to 7·3 atmospheres (Atkins, Biochem. J. 1909, 480).

The chief *uses of eggs* are as an article of food and in the tanning industry. As the supply of new-laid eggs varies with the season, recourse is had to some means of preserving a proportion of those that come into the market at the time of greatest production.

The following is a list of some processes for preserving whole eggs, which have been patented.

Saturating with carbon dioxide (Lake, Eng. Pat. 1653, 1888) ; treating with formaldehyde vapour (Loft, Eng. Pat. 19721, 1915 ; Corden, Eng. Pat. 15206, 1914) ; wrapping air-tight in rubber-coated paper (Jessen, Eng. Pat. 15580, 1891) ; coating with gelatin (Mills, Eng. Pat. 17717, 1891 ; Farquhar and North, Eng. Pat. 15128, 1892 ; Coakley, Eng. Pat. 18816, 1899) ; with gelatinous starch solution (Schultz, Eng. Pat. 1328, 1902) ; with drying oils, wax, or varnish, with or without previous treatment with antiseptics (Stukes, U.S. Pat. 649899 ; Barlow, Eng. Pat. 11054, 1902 ; Lorne, Eng. Pat. 18439, 1901, and 9898, 1901 ; Davis and Metz, Eng. Pat. 105840, 1916) ; with boric acid (Markham, Eng. Pat. 3513, 1895) ; with lime (McArdle, Eng. Pat. 3592, 1892 ; Wilson and Wilson, Eng. Pat. 15461, 1899) ; with sulphuric acid (Reinhardt, Eng. Pat. 18130, 1898 ; Marks, Eng. Pat. 12867, 1903) ; with liquid petroleum (Henderson, Eng. Pat. 101337, 1916) ; and with water-glass (Stead, Eng. Pat. 4910, 1882 ; Rylander, Eng. Pat. 23523, 1901).

The following methods (J. Soc. Arts. 1898, 46, 390 ; J. Soc. Chem. Ind. 1898, 261) were found to keep over 90 p.c. of the eggs in good condition for 8 months : (1) varnishing with vaseline ; (2) keeping in milk of lime ; and (3) keeping in water-glass solution. Of these the last method is the one least open to objection, and is that chiefly used. Eggs preserved in water-glass have a tendency to burst when boiled, but this can be prevented by piercing the shell with a needle.

A Chinese preparation, ' Pidan,' is made from duck's eggs by coating them with a paste obtained by stirring into an infusion of 1¼ lbs. strong black tea, 9 lbs. lime, 4½ lbs. salt, and a bushel of wood ashes. After 5 months they are coated further with rice hulls. The changes which take place were investigated by Blunt and Wang (J. Biol. Chem. 28, 125), who deduced that decomposition of both the egg proteins and lipins had taken place. The values for ash, for total and organic phosphorus and especially for ammoniacal nitrogen, are high.

The contents of eggs may be preserved by heating at 185°F. with a strong solution of a sugar (glucose, maltose, dextrose, &c.), until

the product contains 40–60 p.c. of sugar. It is readily miscible with water, milk, &c., and will keep for some months without deterioration (Fordred, Eng. Pat. 15762, 1894 ; Goodlett, U.S. Pat. 692268).

An important method of preserving the whites and yolks of eggs consists in drying the mixture in a current of air at 37°–40° during 18 hours, powdering the product, and again exposing to dry air. The powder is packed in tins, or can be pressed into tablets, and is quite soluble in water (Foschi, Fr. Pat. 369967, 1906). A similar product is obtained by drying on a hot roller at a temperature above 212°F. (Hatmaker, Eng. Pat. 28, 1905 ; *see also* Eng. Pat. 8743, 1903, for apparatus).

Substitutes for eggs in baking are made from albumin and casein obtained from skimmed milk, sometimes mixed with a proportion of dried egg ; or from maize meal containing sodium bicarbonate and artificial colouring matter (Beythien and Waters, Zeitsch. Nahr. Genussm. 1906, 11, 272 ; Bernstein, Eng. Pat 14336 and 29189 of 1897). An emulsion of sunflower or other oil with blood serum and lecithin has been suggested (Eng. Pat. 100135, 1915).

The eggs used for the treatment of leather, especially the finer sorts of glove leather, are preserved in the liquid state by the addition of salt and borax (Jean, Mon. Sci 1892, 6, 561) Analyses of this material, '*eggio*,' show that it contains 2–5 p.c. more water and 3½–6 p.c. less fatty acid than fresh egg yolk (Boyer, J. Soc. Chem. Ind. 1892, 447) Bein has pointed out that the addition of salt to yolks materially reduces the amount of fat (Bied. Zentr. 21, 138) Rotten eggs could well be used for this purpose, as Cech has found that the available oil is not much diminished in amount, and can be extracted by pressure (J. pr. Chem. [2] 22, 338).

Oil of egg, obtained by extracting yolks with ether, or, better, chloroform, forms about 10 p c. of the egg, and is used in pharmacy in the preparation of ointments and emulsions ; in the leather industry and in tempera painting (Lupus, D. R. P. 187211). It has no medicinal value (Paladino and Toso, Analyst, 1896, 21, 161) It has the following properties : m.p 22°–22·5° ; sp.gr. at 15°, 0·9144 ; acid number, 1·2 ; saponification number, 190·2 ; ether number, 189·0 ; iodine number, 72·1 ; Hehner's number, 95·16 ; Reichert-Meissl number, 0·4 (Kitt, Chem. Zeit. 1897, 21, 303).

Detection, estimation, and analysis.—The presence or absence of egg yolk in pastry can be determined by examination of the fat, there being a great difference in composition and properties between the fat of wheat and of the egg (Spaeth, Zeitsch. Nahr. Genussm. 1896, 10, 171). The phosphorus of the yolk being present chiefly as lecithin, the yolk may be estimated by igniting with sodium carbonate and nitre, determining the phosphoric acid in the residue. 1·129 grams phosphoric acid represent 100 grams yolk (Bein, Ber. 23, 423). The addition of alkali is necessary to prevent loss of phosphoric acid during ignition (Juckenack, *l.c.*). The amount of egg present in pastry, &c., may be determined by the amount of cholesterol present (Cappenberg, Chem. Zeit. 1909, 33, 985). (For methods for the determination of the con-

stituents of egg yolk for commercial purposes, *see* J. Soc. Chem. Ind. 1906, 829.)

EGG ALBUMIN *v.* PROTEINS.

EGG FRUIT. The fruit of *Solanum melongena* (Linn.). A plant of tropical and sub-tropical countries. König gives, as the mean of three analyses—

Water	Nitrogenous matter	Soluble carbohydrates	Fat	Fibre	Ash
93·2	1·1	0·1	3·9	1·2	0·5

An American analysis (Bull. 28, U.S. Dept. of Agric.) shows a somewhat larger amount of carbohydrates (5·1 p.c.), but is similar in other respects.

This plant is sometimes called *Aubergine*. The fruit is used in much the same way as the tomato.   H. I.

EGOLS. A class of antiseptics consisting of the potassium mercury salts of *o*-nitrophenolsulphonic acid, the individual members being termed '*phenegol*,' '*cresegol*,' &c., depending on the phenol from which they are derived. They are reddish-brown powders, readily soluble in water, and are strongly bactericidal (Gautrelet, Compt rend. 129, [2] 113 ; J. Soc. Chem. Ind. 1899, 854) (*v.* SYNTHETIC DRUGS).

EGYPTIAN BLUE. This is a blue colouring matter which was used by the Romans in the first few centuries of the Christian era, but ceased to be manufactured about the time of the invasion of the barbarians. It figures in several beautiful frescoes in the Vatican, and has also been found at Pompeii. Fouqué discovered the composition to be that of a double silicate of calcium and copper $CaO,CuO,4SiO_2$, devoid even of traces of alkali. The substance is crystalline, and is hardly attacked by any chemical reagents, which explains the perfect state of its preservation in the paintings for which it was employed 1900 years ago. It may be prepared at a bright-red heat, but this temperature must not be exceeded, as it is then decomposed into cuprous oxide, *wollastonite*, and a clear light-green glass. The higher the temperature, the more of the latter is formed, and, finally, wollastonite disappears entirely. By the old method of preparation, described by Vitruvius, fine sand and soda are intimately mixed with copper filings, then moistened with water, formed into cakes, and the latter dried. The cakes are then fused in an earthen pot until the blue colour is produced. Fouqué found this method practicable, but used potassium sulphate in preference to soda as a flux. It was not possible to replace chalk or lime by magnesia. The ancient Romans employed a large excess of silica, whilst Fouqué employed more basic mixtures, finally purifying the product with hydrochloric acid. The exquisite colour of this mineral body, the fact that it is absolutely unaffected by moisture, light, and most chemical reagents, as well as the facility and the low price of production, render it desirable that its manufacture should be again resumed (F. Fouqué, Compt. rend. 108, 325–327 ; and J. Soc. Chem. Ind. 8, 291). The conditions of its production have been studied by Laurie, McLintock, and Miles (Proc. Roy. Soc. 1914, A, 89, 418). The French ultramarine works of Deschamps Frères reproduced Egyptian blue by fusing in an ultramarine furnace a mixture of quartz (50 parts),

chalk (21 parts), copper oxide (24·4 parts), and sodium carbonate (4·6 parts), all in the finest powder, and completely free from iron. The product, washed with hydrochloric acid and hot water, had the composition corresponding to Fouqué's analysis, and was in all respects similar to the material used by the Romans (Bock, Zeitsch. angew. Chem. 1916, 29, i. 228).

EIKONOGEN. Sodium salt of 1-amino-β-naphthol-6-sulphonic acid. Used as a photographic developer.

EKSANTALAL $C_{12}'H_{18}O$. Obtained on oxidation by ozone of the sesquiterpene primary alcohol a-santalol $C_{15}H_{24}O$, which, together with the isomeric β-santalol, constitutes 'santalol,' the oil resulting from the hydrolysis of the hydrogen phthalate made from the oil obtained by distilling sandalwood with steam (Semmler, Ber. 43, 1893).

It is dextro-rotatory ($a_D +13·5°$); b.p. $100°-110°$, under 10 mm.; sp.gr. 0·9846 at $20°/20$; n_D, 1·48519.

It gives an oxime, which yields the corresponding nitrile and amine, and gives eksantalol on reduction (Semmler, Ber 41, 1488).

Heated with acetic anhydride and sodium acetate, it forms *enol*-eksantalal acetate

$$C_{12}H_{17}O·CO·CH_3$$
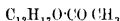
which, on oxidation with potassium permanganate, yields noreksantalic acid $C_{11}H_{16}O_2$ (Semmler, Ber 43, 1722–1725), the methyl ester of which, on reduction by sodium and alcohol, yields noreksantalol $C_{11}H_{18}O$; and this on oxidation in benzene solution with potassium dichromate and dilute sulphuric acid, gives *noreksantalal* $C_{11}H_{16}O$, b.p. $92°–94°/11$ mm ; sp gr. $20°/20°$ 0·9964, n_D 1·48301, $a_D -30·8°$. The *enol*-noreksantalal acetate gives, on oxidation by potassium permanganate, *teresantalic* acid $C_{10}H_{12}O_2$ (Semmler and Zaar, Ber. 43, 1890).

In all three series, containing 10, 11, and 12 carbon atoms respectively, the same tricyclic system is present as exists in a-santalol ; and Semmler (Ber. 43, 1893–1898) assigns to these bodies constitutions based upon the camphene or camphor type, and a-santalol and eksantalal are structurally represented as below :

a-Santalol.

Eksantalal.
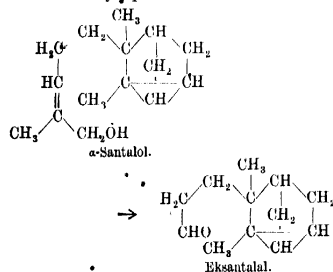
EKTOGEN. Trade name for a mixture of zinc dioxide with zinc oxide and carbonate, used as a surgical dressing.

ELÆOMARGARIC ACID $C_{19}H_{32}O_2$. An acid, melting at 48°, obtained by the saponification of eläocococa oil (Japanese wood oil) with

alcoholic potash, and decomposing the *trielæomargarin* thus formed. The glyceride when first formed is liquid, but on exposure to light gradually solidifies. Isomeric with eläostearic acid, eläoleic acid, and linoleic acid. On exposing an alcoholic solution to light, plates of eläostearic acid, m.p. 71°, are precipitated (Cloëz, Bull. Soc. chim. 1876, 26, 286 ; 1877, 28, 24) ; traces of iodine or sulphur also bring about this change (Maquenne, Compt. rend. 135, 696). Oxidation with potassium permanganate gives rise to azelaic acid, sativic acid, and dihydroxystearic acid (Kametaka, J. Soc. Chem Ind. 1903, 1138 ; 1908, 1120 ; Kit, Chem. Soc. Abstr. 1905, i. 10 ; Maquenne, *l.c.*). Linolic acid also on oxidation yields sativic acid, and on bromination, linolic acid and elaomargaric acid yield the same tetrabromide. Elaostearic acid and linoleic acid yield the same diozonide (Majima, Ber. 1900, 674). Elaomargaric acid and elaostearic acid are converted into elaoleic acid when heated at 180° in sealed tubes (Cloëz, J. 1878, 38).

ELÆOPTENE. The volatile portion of an essential oil, used in contradistinction to the *stearoptene* or solid portion.

ELAÏDIC ACID $C_{18}H_{34}O_2$. A solid stereoisomeric modification of oleic acid, obtained by the action of nitrous acid upon olive oil, saponifying the glyceride (elaidin) so formed, and decomposing the salt by hydrochloric or sulphuric acid. May also be obtained by the action of nitrous acid or of nitric acid (sp.gr. 1·2) (Edmed, Chem. Soc Proc. 1899, 190) upon oleic acid, or by decomposing barium oleate with fuming nitric acid ; m.p. 52° (Saytzeff, Chem. Soc. Abst. 1893, 551). b p. 287 5°–288° at 100 mm. (Krafft and Mordlinger, Ber 1889, 819). Soluble in alcohol and ether. Solutions have an acid reaction. The melted acid gradually absorbs oxygen from the air, and becomes permanently liquid. It may be distilled unchanged under diminished pressure. Heated with potassium hydroxide, it is converted into acetate and palmitate of potassium with evolution of hydrogen.

Elaidic acid dissolved in benzene, toluene, ligroin, or chloroform, and mixed with caustic soda and shaken, gives a brilliant phosphorescence (Radziszewski, Annalen, 203, 305). Hydriodic acid forms an addition compound (iodostearic acid) with elaidic acid (Farb. vorm. Fried. Bayer & Co. D. R. P. 180087; Chem. Soc. Abstr. 1907, i. 380), which, on treatment with alcoholic potash, yields oleic and *iso*-oleic acids (Lebedeff, *ibid.* 1893, 550). On reduction with nickel or copper and hydrogen at 280°–300°, elaidic acid is converted into stearic acid (Sabatier and Mailhe, Ann. Chim. Phys. [8] 4, 319). Treated with dilute solution of potassium permanganate in presence of potash, it is converted into a dihydroxy acid, which differs from the corresponding compound obtained from oleic acid by its lower melting-point (99·5°), and its greater solubility in alcohol and ether, and also into polargonic, azelaic, and oxalic acids (Saytzeff, Ber. 1886, 21 ; Edmed, Chem. Soc. Trans. 1898, 627) ; oxidation with sulphuric acid, however, gives rise to the same dihydroxystearic acid as is obtained from oleic acid under the same conditions (Tscherbakoff and Saytzeff, J. pr. Chem., 1898, 27).

Elaidin, a solid isomeride of olein, is obtained by the action of nitrous acid upon olein,

and is probably a triglyceride $C_{57}H_{104}O_6$. It melts at 36°; is nearly insoluble in alcohol, readily soluble in ether. The *Unguentum oxygenatum* and *U. citrinum* of the pharmacopœias, prepared by the action of nitric acid upon hog's lard, contain impure elaïdin.

ELAIDIN v. ELAÏDIC ACID.

ELALDEHYDE v. ALDEHYDE.

ELARSON. Trade name for strontium chloroarsenobehenolate.

ELATERIN v. ELATERIUM.

ELATERITE. *Elastic bitumen, Mineral caoutchouc.* A fossil resin, somewhat resembling asphalt, found at Castleton in Derbyshire, in France, Switzerland, &c. It is a soft, flexible, elastic, and readily inflammable substance, with a resinous lustre and a dark-brown colour. It is mainly used as an insulator for electric cables. It is rapidly decomposed by strong nitric acid. When boiled with alcohol and alcoholic potassium hydroxide it behaves like beeswax. One sample gave an acid value of 4 9, and saponification value of 56·9, and contained 88·9 p.c. of unsaponifiable matter.

ELATERIUM. The sediment from the juice of the fruit of the *Ecballium elaterium* (Richard), or squirting cucumber. Elaterium is a drastic purgative.

It, and elaterin derived from it, were excluded from the B.P. in 1914. The latter substance is still official in the United States (*Elaterinum*, U.S.P.). Good specimens of elaterium when extracted with chloroform yield 25 p.c. of elaterin, which by recrystallisation is obtained in minute shining six-sided plates. The dose of elaterin is $\frac{1}{16}$ to $\frac{1}{5}$ of a grain, and to it is ascribed the whole of the physiological activity of elaterium. Elaterin is a neutral bitter compound, insoluble in hot or cold water. It is readily soluble in cold alcohol, sparingly in ether. If sulphuric acid be added to a solution of elaterin in melted phenol, a crimson colour is produced which changes to scarlet (Lindo, Chem. News, 37, 35 ; Johannson, Zeitsch. anal. Chem. 24, 154).

On hydrolysis with alcoholic potash, elaterin furnishes acetic acid and an amorphous compound, *elateridin*. Further action of alkali gives *elateric acid*, also amorphous, and melting at 73°–75° (Berg, Bull. Soc. chim. [iii.] 35, 435).

Elaterium of English origin, examined by Power and Moore (Pharm. J. [iv.] 29, 501), was found to contain 5·3 p.c. of moisture and 6·7 p.c. of ash. By a suitable method of extraction, a colourless crystalline product, m.p. 217°,220°, was obtained, corresponding with the elaterin of the pharmacopœias. This was found to be non-homogeneous, consisting of at least two substances, one, *a-elaterin*, melting at 230° with decomposition, and lævo-rotatory, whilst the other, *β-elaterin*, has a lower melting-point, and is dextro-rotatory. Both have the same empirical composition, but the former is physiologically inert, whilst the latter shows marked physiological activity. Examination of commercial elaterin showed that it consists mainly of varying proportions of these two substances, which probably accounts for the marked difference in medicinal value of different samples. a-Elaterin has also been found in colocynth, the dried fruit of *Citrullus colocynthis* (Schraeder) (Power and Moore, Chem. Soc. Trans. 97, 99), and has

been further investigated by Moore (*ibid.* 97, 1797).

According to Berg (Bull. Soc. chim. [iii.] 17, 85 ; [iv.] 7, 385), elaterin does not exist readyformed in the fruit, but is produced after the rupture of the tissues by the action of an enzyme *elaterase* on a glucoside present. The latter consists of a brittle, amorphous powder, and gives the same reactions as elaterin with sulphuric acid and phenol. Power and Moore (Chem. Soc. Trans. 95, 1985), however, on examination of the fresh fruit, failed to confirm this.

G. B.

ELBON. Trade name for cinnamoyl-*p*-hydroxyphenylurea.

ELDERBERRY. The fruit of *Sambucus nigra* (Linn.). The only analysis quoted by König gives, as the composition of the fruit—

Water	Crude fibre	Pentosans
81·9	6·6	1·2

The berries are used for the preparation of a wine and of 'elderberry syrup,' an old-fashioned cordial. From the wine, a brandy is sometimes distilled, which according to analyses by Arnthor and Zink, quoted by König, contains 39·2 p.c. of alcohol (by weight) and has a sp.gr. of 0·836. According to de Sanctis (Gazz. chim. ital. 1895, 25, 49), elder leaves and stems contain conine. Malmejac (J. Pharm. Chim. 1901, 14, 17) attributes the diuretic and purgative action of the bark of the elder to an alkaloid, *sambucine*, a deliquescent bitter substance, yielding the usual alkaloid reactions. He also found elder bark to contain tannin, a resin resembling scammony and a yellowish-red oil possessing a strong odour of elder. Elder pith contains both xylan and araban (Browne and Tollens, Ber. 1902, 35, 1457). The oil extractable from the juice of red elderberries (*S. racemosa*) by ether, is light yellow in colour, has a sp.gr. of 0·9072, solidifies at −8°, and melts at 0° ; contains 6·65 p.c. of free acid (as oleic acid), 0·66 p.c. of unsaponifiable matter, has a saponification number 209·3, iodine number 81·4, and Reichert-Meissl value of 1·54 (Byers and Hopkins, J. Amer. Chem. Soc. 1902, 24, 771).

The leaves of the elder contain a cyanogenetic glucoside, which, under the influence of emulsin, yields dextrose, benzaldehyde, and hydrogen cyanide ; the yield of the last mentioned amounts to 0·126 gram per kilogram of fresh leaves (Guignard, Compt. rend. 1905, 141, 16 ; Bourquelot and Danjou, *ibid.* 59). This glucoside, which has been named *sambunigrin* $C_{14}H_{17}O_6N$, crystallises from ethyl acetate in long, colourless needles, melting at 151°–152°, is readily soluble in water or alcohol, but nearly insoluble in ether (Bourquelot and Danjou, Compt. rend. 1905, 141, 598).

According to Ravenna and Tonegutti (Chem. Zentr. 1910, i. 544) the enzyme which decomposes the glucoside in the plant is not soluble in water. The hydrocyanic acid is present in larger quantities than has hitherto been believed, and is most abundant in the stalks. H. I.

ELECTRARGOL. Trade name for a form of colloidal silver.

ELECTRIRIDOL. Colloidal iridium.

ELECTRO-DEPOSITION and **ELECTRO-PLATING.** Electrolytic processes are now used to a considerable extent in the precipitation

of metals in a reguline form, available for many commercial purposes. Thus the common and more easily corroded metals are coated with thin films of electro-deposited metal of a more permanent and less oxidisable character, in the process of electroplating; for the reproduction of engraved surfaces, type, &c., in electro-deposited copper, electrolysis is applied in electrotyping; and in the deposition of a pure metal from an impure form or a mixture of metals, the principles of electrolysis are applied in the process of electrolytic refining and in chemical analysis.

An electric current passed through solutions of metallic salts brings about decomposition of a particular type, accompanied by the deposition or evolution of the products, or others which may have been formed as the result of secondary changes. When copper sulphate solution is electrolysed with a platinum anode, and any cathode, not ordinarily attacked by this salt, copper is deposited at the cathode, and oxygen and sulphuric acid are formed at the anode, thus:

$$Cu \leftarrow Cu\,SO_4 \rightarrow SO_4 + H_2O = H_2SO_4 + O$$

Deposited on cathode.   Formed at anode.
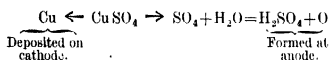
Other metallic compounds follow a similar course. The primary products consist of charged atoms or radicals. These are termed *ions*, and in the process of electrolysis migrate to the electrodes, those to the anode being called the *anions*, and those to the cathode *cathions*. Anions consist of the acidic group of the salt, while the cathions comprise hydrogen, the metals, and basic radicals. At the electrodes, the electrical charges are neutralised, and the substance appears in the nascent form, subsequently being deposited or evolved. Elementary anions, such as chlorine, bromine, and iodine may enter into subsequent secondary changes, while others, such as NO_3, SO_4, $C_2H_3O_2$, &c., react with water, giving generally the corresponding acid, and liberating oxygen. With soluble anodes—those attacked by the anion—solution of the metal takes place, and thus, in a copper solution, a copper anode supplies metal under the best conditions as rapidly as metal is deposited. The strength of the solution is thus maintained, a condition necessary for continuous deposition as required for plating and refining purposes.

The deposition of metals follows the usual law of chemical equivalents as enunciated by Faraday in 1835. The ampere-hour is thus associated with a definite amount of metal, which cannot be exceeded, but may not be attained owing to failure in realising the best conditions. The quantities of metals deposited by the coulomb, ampere-hour, and 746 ampere-hours, are shown in the table on next column.

These amounts, however, can only be deposited when the cathode is surrounded by a considerable amount of strong electrolyte, and only under this condition can the facts of electrolysis be applied, as in the voltameter, to the determination of the number of coulombs passing through a circuit. While for most industrial purposes it is not necessary for the theoretical amount of metal to be deposited per ampere-hour, yet the most satisfactory deposits are,

Metal	Chemical equivalent	Mgs. per coulomb	Grams per ampere-hour	Ozs. (av.) per 746 ampere-hours
Copper (cupric)	31·8	0·329	1·182	31·0
„ (cuprous)	63·6	0·658	2·364	62·0
Gold (auric)	65·7	0·680	2·440	58·6(Troy)
„ (aurous)	197·0	2·040	7·320	176·0 „
Iron	28·0	0·290	1·040	27·3
Lead	103·5	1·070	3·870	101·0
Nickel	29·3	0·302	1·085	28·5
Silver	108·0	1·118	4·025	96·5(Troy)
Tin (stannous)	59·0	0·610	2·190	57·5
„ (stannic)	29·5	0·305	1·095	28·7
Zinc	32·5	0·336	1·210	31·8

in many cases, obtained when this condition is most nearly attained. Failing the full amount of metal per ampere-hour, hydrogen is deposited, and this often leads to a dark powdery deposit unsuitable for most industrial purposes. Such deposits, caused usually by excessive current, are said to be 'burnt.' In some solutions—for example, those of copper, iron, or nickel sulphate —this inferior deposit seems to result from the simultaneously deposited hydrogen due to a weak electrolyte. In other examples, that of the alkaline or cyanide copper bath, it would seem (from the fact that much hydrogen may be deposited without 'burning') more probably due to the deposition of traces of basic compounds with the metal (Bancroft, Trans. Amer. Electrochem. Soc. vi. [ii.] 27). This view is supported by the fact that the presence of substances in the solution, which are good solvents for such basic compounds, prevents 'burning' to a considerable extent. Thus, in the alkaline copper-bath, 'burning' is reduced, and the quality of the deposit improved by the addition of such salts as sodium bisulphite and potassium cyanide. In other examples, notably those of tin and lead, the deposit is much improved by the addition of a trace of a colloid, such as glue or gelatine.

Migration of Ions. It is well known that ions migrate to their respective plates with definite speeds under unit potential gradient. If deposition proceeds more rapidly than this rate of migration, the cathode liquid becomes impoverished of its metal, and this involves a falling off in the ampere-hour yield. The deficiency of metal around the cathode is counteracted to a limited extent by the ordinary process of diffusion, but there is a limit to the rate at which metal may be satisfactorily deposited, unless special steps are taken to make up for this slow migration. Methods of circulation and stirring are based on this fact, and also on the further fact that the heavier solution formed around the anode falls to the bottom of the solution, and, owing to its superior conductance, gives rise to the conduction of an undue proportion of the current and consequently thicker deposits on the portion of the cathode in this heavier layer; hence a limit to the rate at which deposition may be safely allowed to proceed is set, and the time required to deposit a given amount of metal varies correspondingly.

E.M.F. for deposition. With an insoluble anode, a definite minimum E.M.F. is required to maintain electrolysis. Thus, when copper sulphate is decomposed with a platinum anode, the total change is as follows :—

$$CuSO_4 + H_2O = Cu + O + H_2SO_4$$
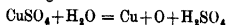
This, as a chemical change, is endothermic, and electrolytically it demands a minimum E.M.F. of about 1·25 volts for its continuance. When a copper anode is used, no change in the composition of the solution occurs. Energy changes at both electrodes are equal and of opposite character, and hence a much smaller E.M.F., viz. that required to overcome the ohmic resistance of the solution, is required. With efficient anode solution and a good conducting electrolyte, such as is obtained in an acidified copper sulphate solution, a P.D. of about 0·3–0·5 volt will maintain a fair rate of deposition. In the case of nickel, where there is usually inefficient anode solution and a poorly conducting electrolyte, a much higher P.D. is required, partly on account of the greater stability of nickel compounds. Figures given, therefore, for P.D.'s at bath terminals are of a very elastic character, depending upon the efficiency of anode solution, strength and temperature of the solution, distance between electrodes, presence or otherwise of conducting substances in the solution, and current density required ; while the conditions controlling the allowable current density at the cathode are chiefly the strength of the electrolyte and its motion.

The **deposition of copper** may be accomplished by simple immersion methods, resulting in a chemical exchange with the more positive metal plated ; thus :

$$\left.\begin{matrix}Zn\\Fe\end{matrix}\right\} + CuSO_4 = \left.\begin{matrix}Zn\\Fe\end{matrix}\right\}SO_4 + Cu$$
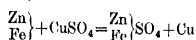
The process is but little used, and then only for very cheap work. Deposits on a surface which is undergoing simultaneous corrosion, cannot be sufficiently adherent to withstand the frictional processes of polishing and burnishing.

The single-cell process, practised at one time, involves the generation of current and the deposition of metal in the same apparatus. The process is illustrated in the Daniell cell, in which, if the copper cylinder is replaced by any conducting substance, copper is deposited.

For the deposition of copper on brass and similar electro-negative metals, and on black-leaded or metallised non-conducting surfaces of wax, guttapercha, plaster, earthenware, &c., the following solution is of wide application :—

Bluestone (CuSO₄, 5H₂O) . .	1½–2 lbs.
Oil of vitriol	¼–½ lb.
Water	to 1 gallon

The composition is variable. Strong solutions admit of more rapid deposition without 'burning,' while the acid imparts conductance. From such a solution deposition can be carried on at the rate of 40 amperes per square foot without stirring, while, with a properly stirred electrolyte, this current density may be increased up to 250 or 300 amperes per square foot.

Previous to deposition, brass is cleaned first in potash (5–10 p.c.) to remove grease. It is then passed through aquafortis to remove scale

of oxide, or tarnish, and, after rinsing, is scoured with pumice or ordinary sand or scratch-brushed. After finally rinsing, it is immersed in the solution, and should be covered immediately. The deposit is pink, though dull. When of sufficient thickness, the work is removed, rinsed, and the dull surface improved by scratch-brushing or polishing.

For deposition upon non-conducting substances such as wax, guttapercha, &c., the following methods may be used :—

(1) *Wax* and *guttapercha.* Thorough yet careful brushing with the finest plumbago causes sufficient to be retained to render the surface conductive. Such surfaces when suspended in the copper solution, receive a deposit beginning at the metal connection, and gradually spreading over the whole surface, the thickness of the deposit not being exactly uniform.

(2) *Plaster of Paris* and *unglazed earthenware* may be rendered conductive by first soaking in linseed oil and allowing to dry. They are thus rendered impervious to the solution; and the skin of dried oil will now retain blacklead, when this substance is applied by gentle brushing, sufficient to impart the necessary conductance.

(3) *Flowers, feathers,* and other delicate objects which will not withstand the pressure of even gentle brushing, may be treated to produce a fine layer of some metal or sulphide on the surface by simple chemical means. A usual method is to paint them or immerse them in a weak solution of phosphorus in carbon disulphide, and, after drying, a brief immersion in silver nitrate solution leads to the precipitation of silver, which imparts the necessary conductance. Again, the object to be treated may first be immersed in silver nitrate solution, and subsequently exposed to sulphuretted hydrogen, which produces a layer of silver sulphide, sufficient to cause the immediate deposition of copper at all points.

A more successful method for wax and guttapercha involves covering these substances with copper by simple precipitation. The substance, usually as a mould or impression of a surface to be reproduced in electrotype copper, is first blackleaded and is then laid face upwards in a solution of copper sulphate. Iron filings are then sprinkled on the surface. The filings in contact with the blackleaded surface produce innumerable voltaic couples, which bring about the deposition of copper quickly and completely. The mould is then rinsed to detach the filings, and placed in the bath, when copper is at once deposited uniformly over the whole surface.

On positive metals such as iron, zinc, tin, Britannia metal, pewter, &c., copper cannot be successfully deposited from the acid sulphate solution on account of the ease with which these metals turn out the copper by simple immersion, and are, moreover, corroded by the acid. A more stable and more satisfactory compound for this class of work is the double cyanide of copper and potassium (CuCN·KCN). Solutions of this compound are usually prepared by (1) dissolving the carbonate in a solution of potassium cyanide ; (2) precipitating the sulphate with ammonia, dissolving the precipitate in excess of ammonia, and decolourising the blue solution with potassium cyanide. Many other

methods are available and are in use. The strength of such solutions may be varied between wide limits up to 4 ozs. (or even more) of metal per gallon. An excess of potassium cyanide is essential, owing to the formation of insoluble single copper cyanide (CuCN) at the anode. The course of electrolysis in such double cyanide solutions (including those of zinc, silver, and gold) is very different from that of the salts of the, mineral acids. In the case of copper, the reaction may be simply represented as follows :—.

Anode		Cathode
	CuCN·KCN	
$\leftarrow$	Cu(CN)$_2$·K$^+$	$\rightarrow$

then :

$$Cu(CN)_2 + Cu = 2CuCN \quad K + CuCN \cdot KCN = Cu + 2KCN$$
(Insoluble)   (deposited)
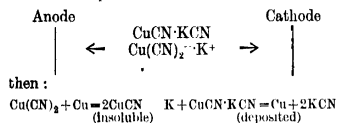
The copper in the salt thus migrates as a complex ion to the anode, and there forms an insoluble compound. This, unless removed, offers considerable resistance, and increases the difficulty of maintaining a normal current Sufficient potassium cyanide for its removal is formed at the cathode, and can be best brought to the anode by stirring, which facilitates the process of deposition by keeping the anode clean. The solution of the anode deposit is more usually accomplished by using an excess of potassium cyanide called 'free cyanide.' From such a solution copper is not deposited upon iron, tin, Britannia metal, pewter, &c., by simple immersion, and only very slightly on zinc. The solution is conveniently used warm, and yields a deposit of copper accompanied by hydrogen, which, as a rule, does not seriously interfere with the physical character of the deposit. The deposit is, under the best qualitative conditions, smoother than that from the sulphate solution, and once the positive metal has been coated in this solution, it may be removed, and, after thorough rinsing, introduced into the sulphate solution for a thicker deposit. The cyanide solution, when strong, and used within certain limits of current density, yields twice as much copper per ampere-hour (viz. 2·36 grams) as the sulphate, the cyanide compound being the monovalent cuprous salt.

Applications of copper deposition.—The metal is most extensively deposited as a covering for more positive and more corrodible metals, and as a preliminary deposit before coating with the more expensive metals. Deposits of copper on iron may then be burnished or polished and the surface improved by metal-colouring, when, by chemical processes, the surface is covered with a uniform film of oxide or sulphide by immersion in solutions producing these compounds, such as the salts of copper and soluble sulphides. Uniform and pleasing effects are readily obtained, and may be rendered more permanent by subsequent lacquering. The metal is also deposited on a considerable scale in the electrotyping process, thin, but rigid reproductions of type, engraved plates and blocks being made in electro-deposited copper, and subsequently strengthened by 'backing' with a lead-antimony alloy, which is then planed down to the required thickness.

Analytically, copper deposition is applied in the separation of this metal from more positive metals in an acid solution with a platinum anode. From a solution of brass in nitric acid, the copper may be most completely deposited without interfering with the zinc. The copper deposit made on a platinum dish or suitable electrode is then weighed, and the zinc obtained by either a chemical or a further electrolytic method (v. ANALYSIS). On a commercial scale, the deposition of copper has been applied by Cowper-Coles to the production of parabolic mirrors for lighthouse work, and to the production of sheet, wire, and tubes. The manufacture of deposited tubes of large diameter has been successfully carried on by Elmore Bros., who arrange an agate burnisher to travel backwards and forwards along the tube during deposition, thereby producing a compact deposit of good mechanical properties. Tubes up to 16 feet long by 8 feet diameter, and weighing more than 3 tons, have been produced by this method. More usually, however, tubes are of smaller dimensions, and are subsequently drawn down or opened longitudinally for the production of sheets. Copper is deposited on a most extensive scale in the refining process, possibly as much as three-quarters of the total output of the metal annually being refined in this manner, using a solution of the sulphate with thick anodes of the crude metal. The crude metal contains up to 1·0 p.c. of impurities. The deposited metal is almost entirely free from impurity. Positive impurities pass into the solution, and are retained there by the application of the principle used in electrolytic analysis. Electro-negative impurities, as silver and gold, pass as chloride and metal respectively into the mud at the bottom of the tank, from which they may be recovered. Tin, antimony, arsenic, and bismuth are prevented from being deposited by a careful control of the conditions, and the sum-total of impurities in the refined metal is usually less than 0·05 p.c.

Deposition of silver. Silver, being an electro-negative metal, is readily deposited by simple immersion. The process is applied commercially under the name of 'whitening.' Solutions for this purpose contain a small proportion of a silver compound, such as chloride or cyanide, dissolved in cream of tartar, sodium chloride, or similar solvent. The deposition on properly prepared work is a case of simple replacement, and only very thin deposits are obtainable by this means. The same materials may also be used in the form of pastes, and rubbed on the prepared work with a wet rag, this method finding application in silvering clock and instrument dials.

Electro-deposition is most frequently practised. For this purpose the nitrate solution is unsuitable on account of its instability, being serviceable only as a voltameter electrolyte where the very electro-negative metal platinum is used. For silvering on more positive metals, those which usually require silver plating, a solution of the double cyanide of silver and potassium is used. This may be prepared from the metal as follows :—

(a) The metal is converted into nitrate, and precipitated with potassium cyanide. When precipitation is just complete, the clear liquid is decanted and the precipitate washed and

subsequently dissolved in more cyanide solution, a further supply of cyanide being added for 'free cyanide.'

(b) Precipitation may be effected by common salt, and the washed chloride dissolved in excess of potassium cyanide.

(c) A silver plate may be made the anode in a 5 p.c. solution of potassium cyanide, using a small copper or carbon cathode contained in some of the solution in a porous cell. The silver dissolves electrolytically, and the process can be continued until sufficient silver has passed into the solution and a good deposit is obtainable from it.

The solution is used cold, and yields a dull deposit of the metal, which may subsequently be scratch-brushed, burnished, and polished. The addition of a small proportion of carbon disulphide (1 oz. in 250 gallons) completely alters the character of the deposit from dull to bright. "Bright plating" is, therefore, much practised. The silver compound in the solution being somewhat unstable, special precautions are necessary before placing work in the solution for deposition. Copper, brass, and nickel silver may be plated directly, though previous to deposition it is common practice to pass such work through a solution of mercury cyanide. This solution can be prepared by treating a soluble mercuric compound with excess of potassium cyanide, or by dissolving the oxide in cyanide. A usual strength is 1 oz. of metal per gallon. From such a 'quicking,' solution a bright deposit of mercury is obtained on brass, copper, and nickel silver by simple immersion, with the advantages that the more negative metal mercury is less oxidisable than copper, &c., and prevents simple immersion deposition of silver when the work is put into the bath, and possibly promotes the adhesion of the subsequently electrolytically deposited silver, by amalgamation. More positive metals, like iron and zinc, are first coppered in the alkaline bath, and subsequently treated as copper. With the lead alloys it is usual to pass them straight from the cleansing processes through a separate silver solution, from which a rapid deposit is first made. This is termed 'striking,' after which the work is transferred to the main solution to complete the deposition.

The current density permissible is controlled largely by the metal content of the solution, Excessive current produces a light-grey, dark-grey, or black deposit, which, being powdery, is unable to withstand the processes of burnishing and polishing.

Silver anodes should be of fine metal, preferably annealed, and, therefore, more susceptible to solution. Their behaviour is an indication of the condition of the solution. If a dull deposit collects upon them, with a falling off in the current, more free cyanide is required to dissolve the insoluble single cyanide which forms upon them. On the other hand, excessive free cyanide unduly promotes the solution of the anode, limits the permissible current density at the cathode, lowers the cathode efficiency, and promotes simple immersion deposition on work which is not 'quicked.' The amount of free cyanide present can easily be determined in this and other cyanide solutions by titration with standard silver nitrate.

The deposition of gold is practised considerably on account of the pleasing colour and permanence of the deposit. Deposition is easy owing to the strong electro-negative character of the metal, and for electro-gilding, as with electro-silvering, cyanide solutions are used. Gold may be applied to metallic surfaces by three methods, viz.: (1) mercurial gilding; (2) simple immersion; and (3) the electrolytic method. Mercurial gilding is used for heavy deposits of gold. An amalgam of gold is first prepared by pouring mercury on to hot gold. Excess of mercury is squeezed through chamois leather, and the pasty amalgam preserved in balls under water. It is applied to the prepared metallic surface with a wire brush, which has first been wetted with a weak solution of mercuric nitrate. This is rubbed on the amalgam and then on to the work, depositing a layer of amalgam. When a uniform coating is obtained, the mercury is expelled in a muffle, and the process repeated for thicker deposits. The dull surface is improved by scratch-brushing. This process is still largely employed.

Simple immersion methods are followed, for mere films of metal, in solutions of very varied composition. A moderately strong solution of sodium pyrophosphate is prepared (5–10 p.c.), and gold chloride added a little at a time. The warm solution at once gives up its metal, but the deposits can, in any case, only be very thin, though they may be thickened somewhat by 'quicking' in a mercury solution and re-immersing in the gold solution.

Gilding with the separate current is largely practised, using a solution prepared by the following or similar methods :—

(1) Making a gold sheet the anode in a cyanide solution (4 ozs. per gallon), using a cathode contained in a porous cell. The process is continued until sufficient metal is lost from the anode or until the solution yields a good deposit.

(2) Precipitating gold chloride with ammonia, avoiding excess, and dissolving the washed precipitate in potassium cyanide solution.

The metal content may vary from a few pennyweights to a few ounces per gallon. The solution is used warm with a gold anode, which is electrolytically corroded, or by a less desirable, though common, method of using an insoluble platinum anode and making frequent small additions of gold chloride. The colour of the deposit varies considerably with the conditions, chiefly that of current. Other conditions, such as temperature, size of anode, distance between electrodes, metal content, also apparently affect the colour: but these varying conditions primarily influence the current. Cold and weak solutions give a pale colour, which may be improved by warming. Excessive current produces darker and foxy deposits, which are, however, improved by scratch-brushing. More satisfactory deposition proceeds when the work is kept in motion. The colour of the deposit is heightened somewhat by a preliminary coating of copper, while a deposit of silver has the reverse effect, though occasionally required. The colour is modified also by the addition of copper and silver cyanides to the solution. Thick deposits are most satisfactorily obtained by occasional scratch-brushing and 'quicking.'

The deposition of nickel is now very largely applied on account of the hardness of the deposit and its permanence, together with the exceptional lustre which can be imparted to it by polishing. The solution most commonly employed is :

Nickel ammonium sulphate	12 ozs.
Water	1 gallon

The conditions which affect the electro-deposition from this solution have been studied by Bennett, Kenny, and Dugliss (J. Phys. Chem. 1914, 18, 373 ; Bennet, Rose, and Tinkler, *ibid.* 1915, 19, 564 ; Hammond, Trans. Amer. Electrochem. Soc. 1916, 30, 103). To this solution, additions are frequently made to increase the conductance, sal-ammoniac or common salt being used. Owing to the fact that no free mineral acid is permissible, and the tendency also to the formation of nickel hydroxide at the cathode, small additions of acids, such as citric, boric, or acetic, are made with varying success. The only modification in the above solution which adds any appreciable advantage, is that of nickel sulphate, which is so much more soluble than the double salt, and from which, therefore, much stronger and therefore better, conducting solutions can be prepared. For thick deposits, Langbein recommends the use of 3 lbs. of nickel sulphate per gallon, with the addition of ethyl sulphate or magnesium ethyl sulphate. On account of the greater stability of nickel compounds and the poor solution of the anodes, and also the absence of free mineral acid, a distinctly higher E.M F. is required than for copper deposition, viz. 5–6 volts for 'striking,' that is, rapidly coating the work with nickel, and then 2–3 volts for depositing the bulk of the metal. The absence of free acid necessitates especial care in the preliminary cleansing processes, most work being finally passed through a weak solution of cyanide (5 p.c.), and quickly and thoroughly rinsed before being put into the vat. The nickel-plating solution is usually worked cold, and is conveniently contained in lead-lined vats. Anodes may be of cast or rolled metal, the cast being much superior, as its porosity assists its corrosion under the influence of the current. Rolled metal is but little attacked by the anion SO_4, and, failing the solution of the anode, sulphuric acid is produced and oxygen evolved ; thus :

$$SO_4 + H_2O = H_2SO_4 + O$$
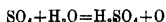
This acidity is to be avoided, and with it there is a diminution in the metal content of the solution which is similarly undesirable. Cast anodes are therefore much more largely used, more uniform conditions being maintained with them. On account of the high E.M.F. used, some hydrogen is evolved at the cathode, though the current efficiency should not ordinarily fall below 90 p.c. Occasional motion of the work is desirable in order to disengage any bubbles which may collect. Once deposition has commenced, the work should not be exposed more than momentarily, otherwise an imperceptibly thin film of oxide will form and almost entirely prevent the adhesion of further deposited metal. In fact, it is considered impossible to successfully deposit nickel on such a surface or on a previous deposit. On this account, previously nickelled work should be entirely freed from its nickel, and, while this may be done by acid solutions, common practice follows the method of polishing, at the same time preparing the surface for the new deposit. Copper and brass work is nickelled directly after the usual cleaning operations, whilst positive metals like zinc and Britannia metal require a previous deposit of copper from the cyanide bath. According to Canac and Tasilly (Compt. rend. 1914, 158, 119), aluminium is readily plated with a durable coating of nickel by first plunging the metal in a boiling potassium hydroxide solution, scrubbing it with milk of lime, followed by steeping in a 0·2 p.c. solution of potassium cyanide for some minutes, after which it is transferred to a bath of 500 grams of hydrochloric acid and 1 gram of iron in 500 c.c. of water. Between each bath it is well washed with water, and then plated electrolytically in a solution of nickel chloride. The success of the plating apparently depends on the use of the ferruginous bath. Iron and steel may be nickelled without coppering, the polished surface being first rendered somewhat dull by scouring with finest pumice. The deposit should be kept bright, and this is attained by a current density not exceeding 5 amperes per square foot. Higher current densities produce dull deposits, tending to become powdery on the edges. The nickel deposit is very hard, and the final lustre is obtained by 'finishing' with Sheffield lime, which produces a highly lustrous surface. In addition to the extensive cycle and motor industry, nickel-plating is applied considerably for small machine parts and instrument work and for 'facing' stereotypes, the deposit being much more durable than the stereotype metal.

The deposition of iron is carried out on lines similar to those for nickel, solutions of ferrous sulphate or ferrous ammonium sulphate being used. These must be entirely free from mineral acid, more so than in the case of nickel, and water should be well boiled before being used, to expel air and prevent the oxidation of ferrous to ferric compounds. Ferric compounds under electrolysis yield little metal, being first reduced to ferrous at the cathode. The process is not much used beyond the application in 'steel-facing' engraved plates. The iron deposit obtained is free from carbon, but is very hard. Anodes of the softest wrought iron containing a minimum of carbon are desirable, and require occasional scouring to remove the layer of insoluble carbon. The deposition of iron has also been used for thicker deposits, which have subsequently been removed and examined to investigate the properties of pure iron, and to more successfully determine the effect of impurities. For 'steel facing,' the engraved plates are cleaned, any scouring being done with only a light brush. The plate is then hung in the bath and covered quickly by 'striking.' Deposition is then continued more slowly for 10–15 minutes. The deposit is very hard and withstands the printing process much better than copper. When the deposit shows signs of wear by the exposure of copper, the metal is simply and readily removed by immersion for a short time in a 5–10 p.c. sulphuric acid. By voltaic

action the iron is soon dissolved from the plate, and, after a light scouring with a fibre brush and subsequent rinsing, the plate is again immersed in the solution to receive a further coating of iron, thus considerably lengthening its life. For a review of the work done in the commercial electro-deposition of **cadmium,** see Mathers and Marble, Trans. Amer. Electrochem. Soc. 1914, 25, 297 et seq.

Of several **cobalt** solutions the following yield the *best results : (1) crystallised cobalt ammonium sulphate, 200 grams per litre of water ; (2) cobalt sulphate, 312 grams ; sodium chloride, 19·6 grams ; boric acid, nearly to saturation ; water, 1000 c.c. From these solutions, cobalt plates on brass, iron, steel, copper, tin, nickel-silver, lead, and Britannia metal, the coating being firm, adherent, hard, and uniform. When polished, the surface, although brilliantly white, has a slight bluish tint. Compared with nickel-plating, the plating with solution (1) is four times, and with solution (2) fifteen times, more rapid, but the voltage required is greater than that used for most nickel-plating baths. Since cobalt is harder than nickel, a much thinner coating of cobalt will offer the same protective coating as a greater weight of nickel deposit ; thick deposits of cobalt are superior in appearance and character to those of nickel (Kalmus, Harper, and Savell, J. Ind. Eng. Chem. 1915, 7, 379 ; Chem. Soc Abst. 1915, 107, ii. 465).

Deposition of alloys. (1) *Brass.* From mixed solutions of zinc and copper sulphates with the addition of acid, copper can be completely deposited free from zinc, this principle being applied in electrolytic analysis and also in refining. With salts more alike in stability, this condition being attained in the double cyanide solutions, the two metals are deposited simultaneously in proportions varying with conditions. The cyanides are invariably used for this purpose, the zinc and copper compounds being used in about the same quantity. The mixed solution may be prepared in many ways, of which the following are in common use :—

(a) Treating solutions of the mixed sulphates with excess of ammonia and adding about 30 p.c. more cyanide (KCN) than is required to decolourise the blue solution.

(b) Preparing a solution of potassium cyanide (1–1½ lbs. per gallon) and saturating about three-quarters of it with the mixed carbonates of zinc and copper, subsequently adding the remaining solution for 'free cyanide.'

The solution may be used warm or cold. If cold, a higher concentration is desirable, and also a smaller proportion of zinc compound. If warm, the zinc compound should be increased and the solution may be safely diluted. Brass anodes are used, which, in a warm solution with a fair proportion of free cyanide, dissolve under the influence of the current. Lack of free cyanide gives rise to the formation of a deposit of the two single compounds on the anode, adding resistance and reducing the current, and thus altering the colour of the deposit. The colour and composition of the deposit vary with several conditions. In general, the conditions which demand a higher E.M.F. give rise to a lighter deposit containing more zinc, whilst those which reduce the resistance of the solution tend to the production of redder deposits containing more copper. Thus more yellow deposits are produced in cold dilute solutions with little free cyanide, whilst the copper in the deposit is increased when the solution is strengthened or warmed, or more free KCN added. The composition of the deposit is controlled also by the proportion of the two metals in the solution, and the fact that from cyanide solutions copper and zinc are ordinarily deposited in the proportion of 63·6 of copper : 32·5 of zinc accounts approximately for the 2 : 1 proportion in deposited yellow brass. The colour of the deposit is lightened by the addition of ammonia or ammonium carbonate, these substances assisting the solution of the zinc compound, which is less soluble than the copper compound, and preventing the formation of basic compounds.

The methods of deposition of brass follow on the same lines as those of copper from the cyanide solution.

(2) Other alloys are deposited to only a very limited extent. The choice of solutions depends upon the ease of mixture of solutions from which the constituents can be separately deposited Thus for bronze, the sulphate, chloride and cyanide solutions, are unsuitable. A satisfactory mixture can be made from the double oxalates of the two metals with ammonium oxalate, the solution being worked warm with a bronze anode. Similarly, a solution from which nickel silver may be deposited may be prepared by mixing the separate double cyanides of copper, zinc, and nickel with potassium cyanide, or by dissolving the alloy in nitric acid, precipitating the mixed carbonates and dissolving the mixture in cyanide. The deposition of these alloys is subject to the same conditions as for brass, attention being paid to those conditions which facilitate the deposition of the more positive constituents, viz. tin, zinc, and nickel

The *electrodeposition of zinc* has of late years been extensively carried on. As a protective coating for iron and steel an electro deposit has great advantages over the ordinary process of galvanising. The sulphate solution is commonly used. In some cases zinc anodes are employed and these to a large extent maintain a constant composition of solution. Other processes employ insoluble anodes, resulting in the formation of sulphuric acid equivalent in quantity to the zinc deposited. The deposition of zinc from such acid solutions demands special conditions, and for general plating purposes the free acid thus formed is neutralised by filtering the liquid through zinc dust. From neutral solutions there is the tendency for the formation of basic compounds leading to the growth of mossy deposits. Such addition agents as glucose beta-naphthol, &c., lead to a considerable improvement in the character of the deposit.

Another extending application of zinc deposition is found in the recovery of zinc from liquors produced by treating certain zinc ores with weak sulphuric acid. The zinc is usually present to the extent of 6–10 p.c. By electrolysis this is reduced considerably, and the acid solution formed by the use of insoluble anodes is then used for extracting the zinc compounds from a further quantity of ore. The process has been applied largely at Anaconda.

Deposition of tin may be successfully carried out from a number of solutions. The chloride yields a beautiful crystalline deposit, but reguline deposits may be obtained from solutions of the stannite, stannate, or double oxalate with ammonium, with ease. They are prepared as follows :—

(1) The hydrate is precipitated from stannous chloride with alkali, and the precipitate dissolved in excess of alkali. .

(2) By converting the metal to hydrated oxide with nitric acid, and dissolving the washed oxide in alkali.

(3) By adding a solution of ammonium oxalate to tin chloride. A white precipitate first forms, and this is soluble in excess.

Solutions containing from 1 to 2 ozs. of metal per gallon are of convenient strength. From these solutions tin may be obtained as a reguline deposit within certain limits of current density Excessive current produces a grey spongy deposit, which may, however, be considerably improved by the addition of a small amount of glue or gelatine, thereby extending the limit of allowable current Solutions of moderate strength yield metal quantitatively, and the anode suffers normal corrosion, maintaining the strength of the electrolyte. The dull white deposit is improved by gentle scratch-brushing with a soft brush. Tin may also be deposited without the current by using an oxalic acid solution to which tin chloride is added The metal is deposited by simple immersion, and the process may be improved by the addition of grain tin with the work, which facilitates deposition by local voltaic action, while tin passes into the solution. The process is hastened by immersing the small work in zinc trays, the zinc passing into the solution as an anode. In this case the solution must be replenished with tin chloride, and rejected when any large amount of zinc has accumulated in it

The **deposition of lead** may be similarly effected from alkaline solutions, which yield reguline deposits, whilst the acetate produces the well-known crystalline deposit. The process has but little application, but more recently the deposition of the metal has been successfully applied by Betts to the refining of the metal The electrolyte is a solution of lead fluosilicate, which may be made by dissolving the oxide or carbonate in the acid. With unrefined anodes the lead passes into solution, whilst silver is retained in the anode mud. Good reguline deposits are obtained by the addition of glue or gelatine in small amount.

More recently, lead perchlorate has been successfully used. Perchloric acid is prepared from the sodium salt with a slight excess of hydrochloric acid. Insoluble sodium chloride is filtered off and the acid liquid evaporated down to 135° C. until excess of hydrochloric acid is expelled. The perchloric acid solution is diluted and neutralised with litharge, a small proportion of the acid being set aside to add to the lead perchlorate solution, so that lead and free acid are present to the extent of about 5 p.c. each. Very satisfactory deposits are obtained from this solution, especially with the addition of peptone in the proportion of 0·05 p.c., and deposits of considerable thickness may thus be produced. With moderate current densities deposition proceeds almost quantitatively, and this with the high chemical equivalent of lead has suggested its use for voltmeter purposes.

A feature of lead deposition is the production of lead peroxide at the anode. This has long been known, and the production of coloured rings and films was first observed by Nobili, in 1826. Thus in a solution of lead acetate, or of litharge in alkali, and a polished anode of nickel or iron, coloured rings are obtained if a wire cathode is held close to the anode. The colours are due to the gradually varying thickness of the film, which brings about interference in the light falling upon them. With anodes of other shapes the colours follow the shape of the anode, though they pass off into a more or less rounded form. These colours are called 'metallochromes.' With excessive current a dull-brown deposit of lead peroxide is at once formed.

Anodic deposition of lead peroxide is also applied in the estimation of small amounts of lead in certain alloys from solutions containing nitric acid.

The **deposition of platinum** is carried out from a solution of the chloride in sodium phosphate. A platinum anode is insoluble and the solution needs the addition of the platinum compound. A brown colour sometimes occurs owing to some of the metal passing into the colloidal form.

Palladium may be successfully deposited from a solution of its double chloride, and the process has been applied by Cowper-Coles for producing a non-corrodible covering for electrolytically deposited parabolic mirrors in copper.

Cobalt deposition follows on lines similar to those for nickel; **mercury**, which may be deposited from the nitrate solution, has been applied to the construction of electrolytic meters, in which a small and definite fraction of the total current is shunted through a cell in which mercury is deposited, the weight of the mercury deposit automatically recording the current passing through the meter, and at constant potential difference the energy absorbed in the circuit.   S. F.

ELECTRUM v. NICKEL.

ELEMI v. OLEO-RESINS.

ELEMI, ESSENTIAL OILS OF, v. OLEORESINS.

ELEMICIN (3 : 4 : 5-trimethoxyallylbenzene). A constituent of the essential oil of elemi has been synthesised by Mauthner (Annalen, 1917, 414, 250) by condensing allyl bromide and pyrogallol-2 : 6-dimethyl ether, which yields 2 : 6-dimethoxyphenyl allyl ether (I.), which, by heating at 220° is converted into 2 : 6-dimethoxy-4-allylphenol (II.) ; this, on methylation, yields elemicin (III.) :—

(I) •   (II)   (III)
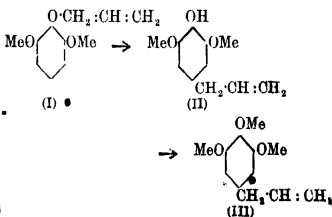
ELEMOL, $C_{15}H_{26}O$, a naturally-occurring monocyclic sesquiterpene alcohol found in Manilla elemi oil; b.p. 152°–156°/17 mm.; D^{20} 0·9411; n_D 1·5030; a_D–5°. Forms a benzoate; b.p. 214°–218°/10 mm.; D^{20} 1·0287; n_D 1·5378; a_D–6°. Elemol, when reduced by means of formic acid, sodium hydrogen sulphate, or zinc-dust, yields *Elemene* $C_{15}H_{24}$; b.p. 115°–117°/10 mm.; D^{20} 0·8797; n_D 1·4971.

Elemol is the first monocyclic sesquiterpene alcohol to be found in Nature or to be obtained artificially (Semmler and Liao, Ber. 1916, 49, 794).

ELIQUATION or **LIQUATION.** A metallurgical term to denote the operation of separating substances by taking advantage of their different fusibilities.

ELLAGIC ACID. Ellagic acid, $C_{14}H_6O_8$, is obtained from numerous tannin matters which contain an ellagitannin by boiling the aqueous extract with dilute sulphuric acid. In many cases it is found in the free state, due probably to the hydrolysis, by fermentation, of the ellagitannin or ellagic acid glucoside originally present, and such a fermentation frequently occurs when aqueous extracts of the tannin matters are allowed to stand for some time.

Divi-divi (*Cæsalpinia coriaria* [Willd.]) (Lowe, Zeitsch. anal. Chem. 1876, 14, 40), myrobalans (*Terminalia chebula* [Ratz.]) (Löwe, *ibid.*), algarobilla (*Cæsalpinia brevifolia*) (Zölfiel, Beilstein, 2, 1085), and valonia (*Quercus aegilops* [Linn.]) yield considerable quantities of ellagic acid, and are the best natural sources of this material. It has also been isolated from oak galls (Chevreul, Ann. Chim. Phys. 1828, [2] 9, 329); oak bark (Etti, Montash 1880, 1, 226); the bark of *Picea excelsa* (Link.) (Strohmer, *ibid.* 1881, 2, 539); pomegranate rind (Rembold, Annalen, 1867, 143, 288); *Quebracho colorado* (Perkin and Gunnel, Chem. Soc. Trans. 1896, 69, 1307); *Arctostaphylos uva-ursi* (Spreng) and *Coriaria myrtifolia* (Linn.) (Perkin, *ibid.* 1900, 77, 424); *Hæmatoxylon campeachianum* (Linn.) (Perkin, *ibid.* 1897, 71, 1137); the fruit of *Cæsalpinia digyna* (Rottl) (Nierenstein, Chem. Zeit. 1909, 87); and the bark of *Terminalia catoppa* (Linn.) (*ibid.*). In fact, ellagic acid probably always occurs, if only in minute quantity, in all plant products which contain gallotannin. Most interesting are the Oriental bezoar stones, concretions which are found in the stomachs of goats and other animals, and consist largely of ellagic acid. These originate, without doubt, from the fact that the animal has fed upon plants in which some quantity of an ellagitannin is present.

Ellagic acid was first discovered by Chevreul (Ann. Chim. Phys. *l.c.*) in oak galls, and more closely examined by Braconnot (*ibid.* 9, 187). According to Pélouze, it possessed the composition $C_7H_4O_4$ (*ibid.* 54, 356); whereas Merklein and Wöhler (Ann. Chem. Pharm. 55, 129), who isolated it from bezoar stones and termed it 'bezoaric acid,' showed that its true formula is $C_{14}H_6O_8$.

The precipitate of crude ellagic acid, which is produced by boiling the tannin extract with dilute mineral acid, is purified by washing with alcohol and subsequent recrystallisation. A similar procedure is also satisfactory with the deposits so frequently produced by fermentation and alluded to above. Ellagic acid is most readily crystallised from pyridine (Perkin and Nierenstein, Chem. Soc. Trans. 87, 1416), and the product, which is either a pyridine compound or contains pyridine of crystallisation, is washed with alcohol.

Löwe (Zeitsch. Chem. 1868, 4, 653) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst and Zwenger (Annalen, 1871, 159, 32) by heating ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmayer (*ibid.* 1871, 160, 55) by heating gallic acid with water and iodine. It is readily produced by oxidising gallic acid dissolved in acetic acid by means of potassium persulphate and sulphuric acid (Perkin and Nierenstein, *l.c.*), and together with flavellagic acid by the addition of potassium persulphate to a solution of gallic acid in sulphuric acid (Perkin, *ibid.* 1906, 89, 251). Under similar conditions, gallotannin produces ellagic acid (Nierenstein, Ber. 1908, 41, 3015; and 1909, 42, 353), and it can also be prepared by boiling the tannin with hydrogen peroxide solution (*ibid.* 1907, 40, 917). Herzig and Bronneck obtained good results by passing air through an ammoniacal solution of gallic acid ethyl ester, and also of gallotannin (Monatsh. 1908, 29); whereas Sisley (Bull. Soc. chim. 1909, [4] 5, 727) prepared ellagic acid from tannin by means of alcoholic potassium hydroxide solution. According to Rupe, a 60 p.c. yield is produced when gallic acid in sulphuric acid solution is oxidised with sodium nitrite (Chemie d. naturl. Farbstoffe, 1909, 2 162).

Ellagic acid crystallised from pyridine forms prismatic needles, which are converted by alcohol into a pale yellow crystalline powder; but when purified by means of its acetyl derivative, the product is almost colourless (Perkin and Nierenstein). It is very sparingly soluble in all the usual solvents, dissolves in alkaline solutions with a pale yellow colour, and from these liquids, when diluted with hot alcohol, is deposited on acidifying in a crystalline condition. When heated it does not melt below 360°; and sublimes at higher temperatures with considerable carbonisation. With nitric acid containing nitrous acid and subsequent dilution, it gives a blood-red colouration (Griessmayer's reaction), and this property, considered at one time to be characteristic, is known to be also possessed by flavellagic acid (Perkin).

According to Merklein and Wöhler (*l.c.*), the alkaline solution of ellagic acid becomes reddish-yellow on exposure to air, and deposits black crystals of potassium glaucomelanate

$$K_2C_{12}H_{14}O_7$$

When boiled with phenylhydrazine in alcoholic solution, or when carefully heated with phenylhydrazine, ellagic acid forms the product $C_6H_5NH·NH_2,C_{14}H_8O_8$, which crystallises in yellow needles, and is readily reconverted into ellagic acid. Ellagic acid gives similar compounds with aniline and quinoline (Goldschmiedt, Monatsh. 1905, 26, 1139).

Tetraacetylellagic acid, $C_{14}H_2O_8(C_2H_3O)_4$, (Barth and Goldschmiedt, Ber. 1878, 11, 846; Schiff, *ibid.* 1879, 12, 1534; Zölffel, Arch.

Pharm. 229, 123), colourless needles, m.p. 343°-346° (Perkin and Nierenstein); *tetrabenzoylellagic acid* $C_{14}H_2O_8(C_7H_5O)_4$, colourless needles (Goldschmiedt and Jahoda, Monatsh. 1892, 13, 151), m.p. 332°-333° (Perkin); *ellagic acid monomethyl ether* $C_{14}H_6O_7(OCH_3)$, yellow crystalline powder (Goldschmiedt, Monatsh. 1905, 26, 1139); *diacetylellagic acid monomethyl ether* $C_{14}H_3O_7(OCH_3)(C_2H_3O)_2$, crystalline powder (Goldschmiedt); *ellagic acid dimethyl ether* $C_{14}H_4O_8(OCH_3)_2$, crystalline powder (Goldschmiedt); and *ellagic acid tetramethyl ether* $C_{14}H_2O_4(OCH_3)_4$, colourless microscopic needles (Goldschmiedt; Herzig and Pollak, Monatsh. 1908, 29, 263), have been described.

Ellagic acid gives the following salts: $KC_{14}H_5O_8$, minute yellow needles (Perkin and Wilson, Chem. Soc. Trans 1903, 83, 134); $K_2C_{14}H_4O_8$, prisms (Merklein and Wohler; Perkin and Wilson): $K_2C_{14}H_4O_8$,KOH, microscopic prisms (Merklein and Wöhler);

$$Na_2C_{14}H_4O_8$$

crystalline powder; $NaC_{14}H_5O_8$,H_2O, yellow needles (Ernst and Zwenger, Annalen, 1871, 159, 32).

The tinctorial properties of ellagic acid are somewhat feeble, but in 1887 it was placed on the market by Messrs. Meister, Lucius, and Brüning, under the name of 'Alizarin Yellow in paste,' and was recommended as yielding, with chromium mordants, greenish-yellow shades of considerable permanence.

Rembold (Annalen, 1867, 143, 288) states that when ellagic acid is treated with sodium amalgam, it gives γ-*hexahydroxydiphenyl*

$$C_{12}H_4(OH)_6$$

three distinct *rufohydroellagic acids* $C_{14}H_{10}O_8$, $C_{14}H_{10}O_7$, $C_{14}H_{10}O_9$, and *glaucohydroellagic acid*; but, according to Nierenstein (Ber 1908, 41, 1649), this latter compound is in reality the pentahydroxydiphenylmethylolid referred to later. By the action of boiling potassium hydroxide solution (Barth and Goldschmiedt, Ber. 1879, 12, 1242), ellagic acid gives *hexahydroxydiphenylenketone* (?) $C_{13}H_4O_7$, by fusion with potassium hydroxide β-*hexahydroxydiphenyl*, and by fusion with sodium hydroxide γ-*hexahydroxydiphenyl*, together with some of the β- compound.

When ellagic acid is distilled with zinc-dust *fluorene* is produced (Rembold, Ber. 8, 1494; Barth and Goldschmiedt, *ibid.* 11, 846; *cf.* also Graebe, *ibid.* 1903, 36, 212).

As a result of their investigation, Barth and Goldschmiedt (*ibid.* 1879, 12, 153) suggested that ellagic acid could be represented by one of the two following formulæ:—

(1) CO $\langle$ C$_6$′(OH)$_3$ / C$_6$′(OH)$_2$ / O / CO

(2) CO $\langle$ C$_6$′(OH)$_2$ / C$_6$′(OH)$_2$ / O / COOH
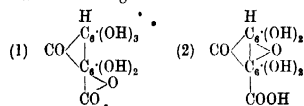
and of these the first was preferable.

Whereas such a constitution requires the presence of five hydroxyl groups, Schiff (Ber. 1879, 12, 1534) considered that acetylellagic acid was $C_{14}H_3(C_2H_3O)_4O_8$, and this was subsequently corroborated by Zölffel (Arch.

Pharm. 229, 123). Schiff, at the same time, proposed two formulæ for ellagic acid:

(1) CO $\langle$ O $\rangle$ C$_6$H(OH)$_2$ / CO $\langle$ O $\rangle$ C$_6$H(OH)$_2$

(2) O $\vert$ CO $\langle$ C$_6$H(OH)$_2$ / CO $\vert$ O $\rangle$ C$_6$H(OH)$_2$
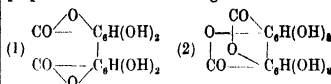
the latter of which is identical with that preferred by Graebe (*l.c.*). In a later investigation, Goldschmiedt and Jahoda (Monatsh. 13, 49), as the result of their preparation of tetrabenzoylellagic acid, were satisfied of the existence in ellagic acid of but four hydroxyls, and consequently adopted their second formula.

Graebe (Ber. 1903, 36, 214), among other criticisms, pointed out that a substance having this constitution, and which may be more clearly written as follows (1):—
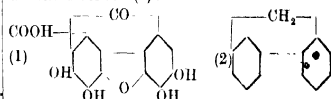
would yield, on distillation with zinc-dust, not fluorene, but an isomeric hydrocarbon (2), if this, indeed, were capable of existence. In the same paper this author announced the interesting fact that diphenylmethylolid
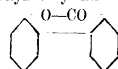
on distillation with zinc-dust, gives not only diphenyl and methyldiphenyl, but also *fluorene*; and in a theoretical discussion of the subject, suggested that Schiff's second formula (given above) most probably represents the true constitution of this substance.

The subject was reinvestigated somewhat later by Perkin and Nierenstein (*l c.*), who, on digesting ellagic acid with boiling potassium hydroxide solution, obtained Barth and Goldschmiedt's so-called hexahydroxydiphenyleneketone $C_{13}H_8O_7$. From this substance a *pentaacetyl* derivative $C_{13}H_2O_7(C_2H_3O)_5$, prismatic needles, m p. 224°-226°, and a pentabenzoyl derivative, $C_{13}H_3O_7(C_7H_5O)_5$, plates, m.p. 257°-259°, were prepared. As, moreover, zinc-dust distillation gave fluorene, there could be little doubt that this compound was in reality *pentahydroxydiphenylmethylolid*, as, indeed, was surmised by Graebe:
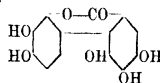
From their results, together with a study of other similar compounds, Perkin and Nierenstein considered that Schiff's formula, and which can be more clearly written thus:
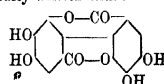
is a correct representation of the constitution of ellagic acid.

Finally, Herzig and Pollak (Monatsh. 1908, 29, 263), by a study of the methylation products of ellagic acid, obtained results further corroborating this constitution.

When Goldschmiedt's tetramethylellagic acid is digested with alcoholic potash and methyl iodide, *diphenyl*-1 : 2 : 3 : 6 : 7 : 8-*hexamethoxy*-5 : 10-*di-carboxylic methyl ester* (m.p. 109°–111°) :

(1)
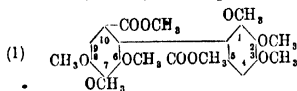
is obtained, together with a small quantity of *diphenylmethylolid*-2 : 3 : 6 : 7 : 8 - *pentamethoxy*-5-*carboxylic acid methyl ester* (2), m.p. 187°–189° :

(2)
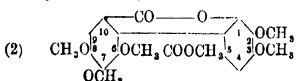
By means of alcoholic potash, these compounds (1) and (2) yield respectively *diphenyl*-1 : 2 : 3 : 6 : 7 : 8-*hexamethoxy*-5 : 10-*dicarboxylic acid* (3), m.p. 238°–240°, and *diphenyl*-2 : 3 : 6 : 7 : 8-*pentamethoxy*-1-*hydroxy*-5 : 10-*dicarboxylic acid* (4), m.p. 200°–203° :

(3)

(4)
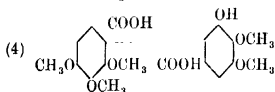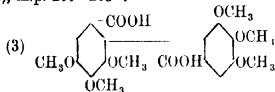
Ellagic acid is probably not a tanning material in the true sense of the term, but is of considerable importance nevertheless in the tanning process. Thus the ellagitannic acid absorbed by the hide is at least in part converted into ellagic acid, and the deposit thus formed adds weight and bloom to the finished article.

Other members of this group have been prepared from *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, proto-catechuic acid, sym. dihydroxybenzoic acid, gallic acid, and from ellagic acid itself. An account of these is given below.

FLAVELLAGIC ACID.

Flavellagic acid $C_{14}H_6O_9$ is obtained in conjunction with ellagic acid when gallic acid is oxidised with potassium persulphate and strong sulphuric acid. By the employment of a dilute acid, flavellagic acid almost free from ellagic acid can be produced, and for this purpose the following process is recommended (A. G. Perkin, Chem. Soc. Trans. 1906, 89, 251) : 20 grams of gallic acid are treated with 160 c.c. of 96 p.c. sulphuric acid, 66 c.c. of water added, and the hot solution thus obtained is cooled to 50°, and maintained at this temperature during the gradual addition of 40 grams of potassium persulphate. A. G. Perkin and F. M. Perkin (Chem. Soc. Trans. 1908, 93, 1194) have obtained the same compound by the electrolytic oxidation of gallic acid in the presence of sulphuric acid,

and more recently Bleuler and Perkin (*ibid.* 1916, 109, 530) have prepared it by heating gallic acid at 110°–120° with arsenic and sulphuric acids.

Flavellagic acid crystallises from pyridine in small yellow prismatic needles which contain pyridine, and do not melt below 360°. With nitric acid containing nitrous acid and subsequent dilution, it gives the blood-red colouration (Griessmayer reaction), which is also produced by ellagic acid. Dilute alkalis dissolve it with a yellowish-green colouration, and by distillation with zinc-dust *fluorene* is produced. *Acetyl-flavellagic acid* $C_{14}HO_9(C_2H_3O)_5$, colourless needles, melts at 317°–319°, and *benzoylflavellagic acid* $C_{14}HO_9(C_7H_5O)_5$, prismatic needles, melts at 287°–289°. Flavellagic acid dyes mordanted woollen cloth shades somewhat resembling but stronger than those produced by ellagic acid.

Chromium.	Aluminium.	Tin.	Iron.
Yellowish-olive.	Pale greenish-yellow.	Pale yellow.	Dark olive-brown.

By the action of boiling 50 p.c. potassium hydroxide solution, flavellagic acid gives *hexahydroxydiphenylmethylolid*
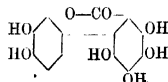
colourless needles (m.p. above 300°). This compound dissolves in solutions of the alkali hydroxides with an orange-yellow tint, and this, on dilution with water and exposure to air, develops a strong bluish-violet colouration. The *acetyl* derivative $C_{13}H_2O_8(C_2H_3O)_6$, colourless prismatic needles, melts at 232°–234°. Flavellagic acid is hydroxyellagic acid, and possesses the following constitution :—
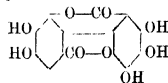
(*cf.* Herzig and Tscherne, Monatsh. 1908, 29, 281).

Flavellagic acid gives with diazomethane the *methyl ether* $C_{14}HO_4(OMe)_5$, m.p. 245° ; and this is converted by methyl iodide and potassium hydroxide into *methyl*-3 : 4 : 5 : 6 : 2′ : 3′ : 4′-*heptamethoxydiphenyl*-2 : 6′-*dicarboxylate*

$$C_{12}H(OMe)_7(CO_2Me)_2$$

m.p. 83°–87°. The latter, on hydrolysis with potassium hydroxide, yields the *acid*

$$C_{12}H(OMe)_7(CO_2H)_2$$

m.p. 163°–167°, in the anhydrous condition. From water it crystallises with $1H_2O$ and then melts at 95°–100° (decomp.) (M. von Bronneck, Monatsh. 1908, 29, 281).

When gallic acid 3 : 4-dimethylether, or gallic acid trimethylether is oxidised by means of potassium persulphate and sulphuric acid at 45° (Herzig and Schmidinger, Monatsh. 1910, 31, 918), *flavellagic acid tetramethylether*
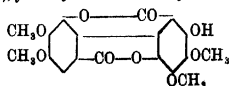
yellow needles, m.p. 270°-271°, is produced, the acetyl derivative of which melts at 270°-271°. By means of methyl sulphate and potassium hydroxide, the heptamethoxy compound is obtained.

CŒRULEOELLAGIC ACID.

Cœruleoellagic acid is prepared by heating ellagic or flavellagic acid (1 part) with sulphuric acid (monohydrate'10 parts) to 200° and allowing the temperature to fall to 185°-190° and remain there for 30 minutes. The product isolated by pouring into water is purified by conversion into its acetyl derivative, and this is subsequently hydrolysed by means of sulphuric acid in the presence of acetic acid. It may also be obtained by the oxidation of ellagic or flavellagic acids (1 part) in sulphuric acid solution (10 parts) with arsenic acid (1 part) at 100°-130° (Perkin, Chem. Soc. Trans. 1916, 109, 529).

Cœruleoellagic acid, $C_{14}H_8O_{10}$, separates from hot pyridine in small pale yellow prismatic needles which melt above 360° and are very sparingly soluble n the usual solvents Concentrated solutions of the alkali hydroxides dissolve it with a greenish-yellow colour, which on dilution become green and finally of a blue colour, and these changes appear to arise from oxidation. Sodium and potassium carbonate solutions also give blue liquids. On distillation with zinc-dust fluorene is produced

Acetylcœruleoellagic acid, $C_{14}O_{10}(C_2H_3O)_6$, colourless needles, m.p. 330°-332°, and *benzoyl-cœruleoellagic acid* $C_{14}H_{10}(C_7H_5O)_6$, m.p. 343°-345°, have been prepared The latter is more sparingly soluble in benzoic anhydride than the corresponding derivative of flavellagic acid, and this property provides a means for the separation of the two substances.

By digestion with 50 p.c. potassium hydroxide solution diluted with its own volume of alcohol, cœruleoellagic acid gives a compound $C_{12}H_{10}O_8$, evidently *octohydroxydiphenyl*. This consists of an almost colourless crystalline powder, soluble in dilute potassium hydroxide solution, with a reddish-violet colouration which becomes brown on exposure to air. The *acetyl* derivative $C_{12}H_2O_8(C_2H_3O)_8$, forms colourless needles melting at 177°-178°.

The constitution assigned to cœruleoellagic acid is as follows :—
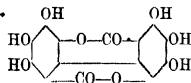
a formula which represents it as either a dihydroxy-ellagic or hydroxy flavellagic acid.

Cœruleoellagic acid possesses well-marked dyeing properties of a similar character, though more strongly developed than those of ellagic and flavellagic acids, and may have practical utility. Owing to its sparing solubility it gives the best results in the paste form. The following shades are obtained by the employment of mordanted woollen cloth :—

Chromium.	Aluminium.	Tin.	Iron.
Deep olive-yellow.	Greenish-yellow.	Dull yellow.	Greenish-black.

In the case of the aluminium mordant the employment of chalk in the dye-bath exerts a detrimental effect.

CATELLAGIC ACID.

Schiff (Ber. 12, 2590) on heating protocatechuic acid with arsenic acid, obtained a substance which he named *catellagic acid*, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. Perkin and Nierenstein (Chem. Soc. Trans. 1905, 87, 1417) obtained a similar substance by the oxidation of protocatechuic acid, and also parahydroxybenzoic acid with potassium persulphate and sulphuric acid. According to the latter authors, catellagic acid $C_{14}H_8O_6$ crystallises from pyridine in colourless needles, which melt above 360°, and sublime with but moderate carbonisation at higher temperatures. Solutions of the alkali hydroxides dissolve it with a pale yellow colour, and with nitric acid it gives a magenta coloured liquid. *Diacetyl-catellagic acid*, colourless prismatic needles, melts at 322°-324°.

Catellagic acid, by distillation with zinc-dust, gives *fluorene*, and is closely related to ellagic acid. Its constitution (Perkin and Nierenstein) may be expressed as follows :—
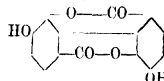
From the oxidation products of parahydroxybenzoic acid, Perkin and Nierenstein isolated, in addition to catellagic acid, a second compound $C_{14}H_8O_6$, colourless needles, m.p. above 360°. This, which gives the diacetyl derivative $C_{14}H_6O_6(C_2H_3O)_2$, colourless needles, m.p. 267°-268°, and by distillation with zinc-dust fluorene, possesses the formula :
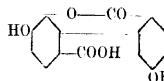
and evidently originates from the interaction of one molecule of protocatechuic acid and one of parahydroxybenzoic acid.

METELLAGIC ACID.

Metellagic acid (Perkin and Nierenstein, Chem. Soc. Trans. 1905, 87, 1425) is obtained in small amount together with other substances by oxidising metahydroxybenzoic acid in sulphuric acid solution with potassium persulphate at about 30°. The product is fractionally crystallised from acetic acid, the second crop acetylated, the acetyl derivative thus obtained purified by repeated crystallisation from acetic anhydride and hydrolysed with sulphuric acid in the usual manner.

Metellagic acid $C_{14}H_8O_8$ crystallises from acetic acid in colourless needles which readily sublime at high temperatures. With caustic alkaline solutions it behaves similarly to catellagic acid giving a yellow colour which is discharged on heating. Distilled with zinc-dust a small quantity of a crystalline hydrocarbon is produced which appears to be identical with fluorene. *Acetylmetellagic acid* $C_{14}H_4O_8(C_2H_3O)$ crystallises in colourless leaflets, m.p. 269°-271°.

The reactions of metellagic acid are in harmony with those required by a member of the ellagic acid series, and the following formula assigned to it is probably correct :—
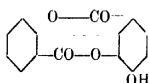
In the mother liquors obtained during the purification of acetyl metellagic acid, a second acetyl compound, m.p. 237°–243°, was isolated. Thus on hydrolysis gave a substance crystallising in glistening yellow needles, the nature of which has not been ascertained.

By the oxidation of suitable hydroxybenzoic acids, a series of hydroxydiphenyldimethyloid derivatives have thus been prepared, viz. :—

Metellagic acid $C_{16}H_8O_4(OH)$
Catellagic acid $C_{15}H_4O_4(OH)_2$
Resoflavine $C_{14}H_2O_4(OH)_3$
Ellagic acid $C_{14}H_2O_4(OH)_4$
Flavellagic acid $C_{14}HO_4(OH)_5$
Cœruleoellagic acid $C_{14}O_4(OH)_6$

A. G. P.

ELLAGITANNIC ACID. A tanning principle present in divi-divi (Löwe, Frdl. 14, 35); in algarobilla (Zölffel, Arch. Pharm. 229, 123); in myrobalans (Lowe, *l.c.* 44; Zölffel, *l.c.*); and probably to some extent in all plant products which contain a gallotannin (*v.* ELLAGIC ACID).

According to Lowe, the molecule of ellagitannic acid contains 5 hydroxyl groups replaced by acetyl. It gives precipitates with gelatin, albumen, alkaloids, tartar emetic, and a nearly black precipitate with ferric acetate. Its alcoholic solution gives, with lead acetate, a yellow precipitate.

Zölffel (*l.c.*) considered it a sugar-free tannic acid of the formula

$C_6H_2(OH)_3COO \cdot C_6H_2(OH)_2COOH$
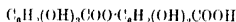
whereas Perkin and Nierenstein (*l.c.*) suggested it to be a glucoside or a condensation product of two molecules of gallotannin.

Nierenstein (Ber. 1910, 43, 1267) has obtained it in a pure state by repeated treatment of the crude substance from myrobalans with alkali and ethyl chloroformate, and then decomposing with pyridine according to Fischer's method; and gives its formula as

$C_{26}H_{28}O_{19}, 3H_2O$
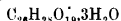
It crystallises from a mixture of pyridine and acetic acid in pale-yellow plates, which, after sintering at 300°–306°, melt at 329°–336° $[a]_D^{17} + 18·02°$. So obtained, it readily yields ellagic acid with dilute sulphuric acid, but is not decomposed by 10 p.c. sodium carbonate solution. As it is hydrolysed by emulsin to luteoic acid, Nierenstein considers it to be a glucoside of this compound (*v.* TANNINS).　　　A. G. P.

ELUTRIATION. The separation of the lighter from the heavier particles of a powder by washing and decantation.

EMANIUM *v.* ACTINIUM.

EMBARIN. Trade name for sodium mercuri-salicylsulphonate.

EMBELIC ACID. The active constituent of the fruit of the Indian plant *Embelia ribes*

(Burm.) (nat. ord. Myrsineæ). Employed as an anthelmintic.

EMBOLITE. Native silver chlorobromide containing chlorine and bromine in indefinite proportions. It is the commonest of the horn-silvers or cerargyrites (*q.v.*), occurring as compact horn-like masses or as small, indistinct cubic crystals of a greenish-grey colour. Frequently a small amount of iodine is also present, and the formula is Ag(Cl,Br,I); the colour of this iodembolite variety is usually greenish-yellow to orange-yellow. Large quantities have been mined with other ores of silver in Chile, Mexico, and Broken Hill in New South Wales. (*V.* Prior and Spencer, Min. Mag. 1902, 13, 174.)

L. J. S.

EMERALD *v.* BERYL, and GLUCINUM.

EMERALD GREEN. *Hydrated chromium sesquioxide* (*v.* CHROMIUM); also applied to *Schweinfurth green* (*v.* art. ARSENIC; also PIGMENTS).

EMERALD-NICKEL *v.* ZARATITE.

EMERALD, ORIENTAL, *v.* CORUNDUM.

EMERY. (*Émeri*, Fr.; *Smirgel, Schmirgel*, Ger.) An impure variety of corundum. It is, however, more of the nature of a rock, rather than a simple mineral, consisting essentially of a fine-grained aggregate of corundum (50–60 p.c.) and magnetite (30–40 p.c.). Several other minerals are also present in smaller and variable amounts. Hæmatite and limonite are present as alteration products of the magnetite; and others, such as diaspore, margarite (emerylite), muscovite, kyanite, have probably been derived from the corundum. In addition, there may also be tourmaline, chloritoid, biotite, staurolite, rutile, idocrase, pyrites, iron-spinel (hercynite), &c. The material is dull black, dark grey, or bluish-black, and has much the appearance of a fine-grained iron-ore; sp.gr. 3·75–4·31. It is massive and opaque, breaking with a more or less regular fracture, and is magnetic. The abrading power (measured by the amount of glass abraded by a given weight of emery in a certain time) ranges from 65 to 32, as compared with sapphire at 100. These values are only roughly proportional to the amount of alumina (corundum) present in the mixture, depending also to some degree on the texture of the material.

The analyses on next page are of material from Naxos, I–IV (I and II, the extremes as regards the amount of alumina of seven analyses by Oser, quoted by S. A. Papavasiliou, 1913; III and IV, by E. Ludwig, quoted by G. Tschermak, 1894); Asia Minor, V, by R. Kramer, 1907; VI, Peekskill, New York, by G. H. Williams, 1887. Several older analyses have been published by J. L. Smith (Amer. J. Sci. 1850, 1851, 1866), and by R. Jagnaux (Bull. Soc. Min. France, 1884).

Analysis III corresponds with the mineral composition : corundum 52·4, magnetite 32·1, tourmaline 11·5, muscovite 2, margarite 2 p.c.; and IV with : corundum 50, magnetite 33, tourmaline 9, chloritoid 4, muscovite 3, calcite 1 p.c.

The only sources of supply are Greece, Asiatic Turkey, and the United States. The deposits in the island of Naxos in the Grecian archipelago have been known since remote times. Here, on the north-east side of the

	I.[1]	II.	III.	IV.	V.	VI.[2]
Al₂O₃	66·16	60·05	57·67	56·52	60·10	46·53
Fe₂O₃	24·27	24·03 }	33·36	34·65	33·20	41·29
FeO	3·48	4·02 }				
MnO	0·25	0·85	—	—	—	—
CaO	1·62	1·51	0·43	0·90	0·48	—
MgO	0·38	1·05	0·83	0·43	—	9·43
K₂O	—	·—	0·31	0·40	—	—
Na₂O	—	—	n.d.	0·60	—	—
SiO₂	3·23·	5·09	5·64	5·45	1·80	2·42
TiO₂	—	—·	n.d.	n.d.	—	0·51
B₂O₃	—	—·	4·15	0·88	—	—
H₂O	0·37	3·67	0·70	0·42	5·62	—
	99·76	100 27	100·09	100 25	101·20	100·19
Sp.gr.	4·06	3·84	3·71	3 98	—	—

island, the emery occurs as irregular beds and lenticular masses in crystalline limestone (marble), associated with crystalline schists and intruded by granite. Large isolated blocks also occur weathered out on the surface. The methods of mining are very primitive, and resort is made to the old method of fire-setting, the surface of the rock being heated by fires and suddenly cooled by water to develop cracks. The production is the monopoly of the Greek government, and amounts to about 10,000 tons per annum. Emery also occurs on the neighbouring islands of Irakha, Sikinos, Paros, and Amurgos, but these deposits are not worked. (On the Naxos deposits, v W. H. Cottrell, Foreign Office Rep., Miscell. Ser. No. 368, London, 1895; G. Tschermak, Min. Petr. Mitt. 1894, xiv. 311; S. A. Papavasiliou, Zeits. Deutsch. Geol. Gesell. 1913, lxv. 1-123.)

The important deposits in western Asia Minor, around Smyrna, were discovered by J. Lawrence Smith in 1847. Here also the emery occurs as lenticular bodies in bluish crystalline limestone, associated with mica-schist, gneiss, and granite; and as loose blocks weathered out in the reddish surface soil. The principal mines are situated on the Gume Dagh or Messogis Mountain in the Aidin district (E. of Ephesus and S.E. of Smyrna). Others are near Mausa (the ancient Magnesia), near Kula and Adula (N. of Ala-Shehr=Philadelphia), and on the neighbouring islands of Samos and Nikaria. The output of 20,000 to 30,000 tons per annum is shipped from Smyrna. (On the Asia Minor deposits, v. J. L. Smith, Amer. J. Sci. 1850, 1851; and Original Researches in Mineralogy and Chemistry, 1884; R. Krämer, Kleinasiatische Schmirgelvorkommnisse Inaug.-Diss. Leipzig, Berlin, 1907.)

In the United States, deposits have been worked at Peekskill in Westchester Co., New York, occurring here as segregations in gabbro; and in amphibolite-schist at Chester in Hampden Co., Massachusetts. The annual output amounts to only about 1000 tons, and that from Chester has now fallen off. (On the United States occurrence, v. G. P. Merrill, The Non-Metallic Minerals, 2nd edit. New York, 1910.)

An abrasive material mined at Wildenreuth and other places in Bavaria under the name of emery (Schmirgel, Ger.) is really a mixture of garnet and quartz. In the trade the name emery has also been applied to the refuse from cutting gems and from gem-washings.

¹ Also Cr₂O₃ trace.   ² Also P₂O₅ trace, S 0·01.

In the preparation of the material for the market, after being carefully hand-picked at the mine, it is crushed under stamps and sorted into various grades of fineness through wire sieves. The finest 'flour of emery' is prepared by washing and elutriation. Emery powder is used by lapidaries and stone workers; for polishing plate glass and grinding lenses. In the form of emery paper, emery cloth, and emery sticks, the powder is fixed by means of glue. For emery wheels the powder is mixed with a cementing material, such as shellac, sodium silicate, or vulcanite; or it is baked with loam or kaolin and thus embedded in terra-cotta or porcelain. Such wheels are much used by lapidaries and dentists, and for grinding and polishing metals, &c. Attempts have been made to use pieces of emery, in place of diamond, in the crowns of rock-drills. (On the technical uses of emery, v. A. Haenig, Der Schmirgel und seine Industrie, Wien, 1910.)   L. J. S.

EMETAMINE v. IPECACUANHA.

EMETINE v. IPECACUANHA.

EMIN RED v. PRIMULINE.

EMODIN v. GLUCOSIDES; RHUBARB; SYNTHETIC DRUGS.

EMPRESSITE. A silver-tellurium mineral AgTe, discovered in the Empress-Josephine mine, Kerber Creek, Colorado, associated with galena and native tellurium. Lustre, metallic; streak, greyish-black; fracture, conchoidal; hardness, 3–3 5; sp.gr. 7·51 (Bradley, Amer. J. Sci. 1914, 38, 163).

EMPYROFORM v. SYNTHETIC DRUGS.

EMULSIN. The term 'emulsin' was applied originally to the enzyme or mixture of enzymes, present in bitter and sweet almonds, which hydrolyses amygdalin to glucose, benzaldehyde, and hydrogen cyanide. The same enzyme was shown subsequently to hydrolyse many natural glucosides as well as the synthetically prepared β-glucosides, though it was entirely without action on the stereoisomeric α-alkylglucosides (Fischer, Zeitsch. physiol. Chem. 1898, 26, 60). The name is now used to comprise all enzymes which hydrolyse β-glucosides. Such enzymes are widely distributed in plants: besides the kernels of fruits, they also occur in the leaves and young twigs of the higher plants, in most mould fungi, especially in Polyporus species parasitic on trees, and in bacteria. Henry and Auld (Proc. Roy. Soc. 1905, B, 76, 568) have identified emulsin as present in yeast.

β-Glucosides are also hydrolysed by certain animal extracts, e.g. intestinal mucous membrane, a fact which is taken to indicate the presence of emulsin.

There are, however, well-marked differences in the number of substances which these various emulsin preparations are able to hydrolyse, and the investigations of Armstrong and others (Chem. Soc. Proc. 1910, 334) indicate, that whilst the leaf enzyme (emulsin) is, as a rule, a specific for the glucoside normally occurring in the particular plant, the seed enzyme, especially that of the almond, is able to attack a number of glucosides. For this reason almond emulsin is considered to be a mixture of several closely related enzymes. According to H. E. and E. F. Armstrong and Horton (Proc. Roy. Soc. 1908. 80, 321), it contains a β-glucase

proper, which attacks β-glucosides; a *cyanase*, which eliminates hydrogen cyanide from amygdalin; an *amygdalase*, splitting off glucose from amygdalin; and a *lactase*, acting on milk sugar (*cf.* Rosenthaler, Arch. Pharm. 1910, 240, 105).

Almond emulsin hydrolyses β-glucosides and also the disaccharides, lactose, gentiobiose, cellose, and melibiose. It further hydrolyses the synthetical β-methylgalactoside. The emulsin of *Aspergillus niger*, on the contrary, has no action on lactose or on β-galactosides. In referring to emulsin, it is therefore advisable to specify the source of the enzyme.

Preparation.—Ground sweet almonds from which the fat has been expressed are macerated with water and a little toluene or chloroform at the ordinary temperature for 12–24 hours. The liquid is expressed through a cloth, protein precipitated with a few drops of acetic acid, and the clear filtrate precipitated with alcohol added 50 c.c. at a time till no further precipitate is formed. The liquid is decanted and the precipitate rapidly washed with absolute alcohol and ether to dehydrate it, and dried in a vacuum. Alternatively the original precipitate may be collected on a filter paper, dried roughly on bibulous paper, and dissolved in water in a closed bottle, to which a little toluene is added. The clear solution so obtained is very active, and retains almost constant activity for many months. It is essential to carry out this preparation as rapidly as possible.

The dried enzyme is a soft, white powder, giving most of the reactions of proteins, but losing these on purification. Its chemical nature has not been the subject of any detailed investigation. Active preparations are to be obtained in commerce.

Emulsin exhibits maximum activity in neutral solution. Alkali stops the action; small quantities of acids usually increase the activity, owing to their effect in neutralising alkaline impurity.

Experiments with emulsin are usually carried out at about 37°; the optimum temperature is 45°. Emulsin is less resistant to destruction by heat in presence of alcohol below 50 p.c., but above this point the reverse is the case, owing to the fact that in stronger alcohols the enzyme is precipitated, and in this condition is more resistant to heat. In sterilising plants containing enzymes it is best to use alcohol of such strength as to produce a liquid containing about 60 p.c. of alcohol (Bourquelot and Bridel, J. Pharm. Chim. 1913, 7, 65).

Emulsin. is detected qualitatively ,by its action on amygdalin, liberating hydrogen cyanide. The activity is tested quantitatively either against amygdalin or salicin, by measuring the amount of sugar formed in a given time.

Emulsin is also able to bring about synthetic change (Armstrong, Proc. Roy. Soc. 1905, B, 76, 592; van't Hoff, Sitzungsber. K. Akad. Wiss. Berlin, 1910, 48, 963). Emulsin exhibits hydrolytic activity in alcoholic solutions. Although unable to hydrolyse salicin in presence of 95 p.c. alcohol, it becomes active in 90 p.c. alcohol, hydrolysis continuing slowly until 37 p.c. of the glucoside has been decomposed. As the strength of the alcohol is diminished equilibrium is more rapidly attained, and a greater proportion of the salicin undergoes hydrolysis (Bour-

quelot and Bridel, Compt. rend. 1912, 154, 944). Similarly, emulsin is inactive when suspended in solutions of glucosides in acetone or ethyl acetate, but becomes able to effect hydrolysis when 10 p.c. of water is added to the acetone or the wet ester is used. When emulsin acts on a solution of glucose in 85 p.c. alcohol, the corresponding β-methyl or β-ethyl glucosides are formed, the same equilibrium point being reached in solutions containing originally glucose or alkyl glucoside. The more dilute the alcohol the greater is the hydrolysis and the less the synthesis (Bourquelot and Bridel, Compt. rend. 1912, 155, 319). The position of the equilibrium is independent of the quantity of emulsin added and of the temperature, but it varies with the strength of the alcohol and with the amount of glucose present. The property of emulsin to facilitate synthesis has been utilised by Bourquelot to prepare a large number of glucosides of the alcohols, including such substances as geraniol and glycol, and also the corresponding galactosides.

The emulsin contained in a number of plant preparations is able to hydrolyse *dl*-benzaldehyde cyanohydrin, and also to synthesise this compound from benzaldehyde and hydrocyanic acid. In some cases the synthesis is asymmetric, and an optically active cyanohydrin is formed (*cf.* Rosenthaler, Arch. Pharm. 1913, 251, 56).

(For a list of the glucosides attacked by emulsin, *v.* GLUCOSIDES.)   E. F. A.

ENAMEL BLUE. *Cobalt blue* (*v.* PIGMENTS).

ENAMELS are vitreous compositions capable of adhering by fusion to the surface of metal or of pottery. The base of the enamel is generally a colourless glass, in which are suspended particles of an opaque metallic oxide or salt, generally stannic oxide. Up to about 900°, tin dioxide exists finely suspended in the enamel, but at a higher temperature combination or solution may occur and opacity is diminished. Titanic oxide has been used in place of stannic oxide, and antimony compounds have been employed. Opacity may also be obtained by the use of arsenious oxide, calcium phosphate, cryolite, or fluorspar. A preparation known as 'artificial cryolite' sometimes replaces the mineral. When bone ash is used, a little nitre may be added to remove the grey colour; the nitre also prevents reduction of the lead. The vitreous base of most enamels is a glass containing much lead, but when the presence of lead is objectionable, as in enamelled vessels for culinary purposes, soda- and potash-glasses should be used. If great fusibility be required, it may be secured by the association of borates with the silicates. Borate enamels are very hard, but are deficient in elasticity, and may be affected by moisture. Colour is imparted to the enamels by the introduction of various compounds, generally metallic oxides, the use of which, in many cases, has been known from remote ages. Percy's analyses of the enamelled bricks of Babylonia (*circa* 700 B.C.) showed that a dense white was obtained by the use of stannic oxide; a rich yellow by means of antimony, apparently in the form of lead antimoniate ('Naples yellow'); and a deep blue by copper, probably introduced as oxide, but existing in the enamel as a copper sodium silicate. The ancient Egyptian blue enamel, or glaze,

contains a definite copper calcium silicate, forming crystals remarkable for their intense pleochroism, to which Fouqué gave the name of *vestorien* (Bull. Soc. Fr. Min. [12] 1889, 36) (*v.* EGYPTIAN BLUE). The ancient Egyptians seem to have been ignorant of the art of enamelling on metal.

The enamelling of pottery is a simple operation, since it consists in the mere fusion of an opaque glaze on to the surface of the ware. But the application of a vitreous body to a metallic surface is less easy, and it is to this process that the term 'enamelling' is sometimes restricted, while the works of art produced by enamelling on metal are themselves known as 'enamels.'

The most ancient enamels found in North-Western Europe are referable to the prehistoric Iron Age, sometimes distinguished as Late Celtic. In these ancient enamels, brilliantly coloured opaque glass is embedded in cells or shallow cavities in bronze : it is probable that the vitreous material was applied as a powder, mixed with a vehicle so as to form a paste, and then heated sufficiently to cause its fusion, and thus secure firm attachment to the metal.

A similar method, known as *champ levé* enamelling, was extensively employed at a much later date in Germany and at Limoges in France —a town which for centuries was the chief centre of artistic enamelling. In this process the design is traced on a plate of copper or bronze, and all the parts to be enamelled are excavated by the graver ; these hollows are then filled with enamel, which is afterwards fused, and the entire surface is finally ground smooth. The design thus appears in permanent colour, each tint being defined by ridges, or separated by areas, of metal which are the elevated parts of the original ground. The exposed metal is sometimes gilt.

Another and probably older method of inlaid enamelling is that known as *cloisonné* work. Here the design is outlined by strips of metal fixed to the metallic base, and the spaces between these bands are filled with enamel, which is then fused and the surface ground down. Each coloured area is, therefore, sharply separated from its neighbour by the edge of the metal fillet. Of this character were the early Byzantine enamels, which were generally executed on plates of gold. The Chinese have for many centuries (at least since the 13th) been extremely skilful in this work, and the Japanese have applied a similar method to the ornamentation of porcelain. The Japanese attach the cloisons to the base with a gummy cement, and even when the ground is a metal, they generally use no solder. In some *cloisonné* work the surface is not ground down, so that the fillets stand in relief above the general surface of the enamel.

The use of transparent enamels for the ornamentation of metalwork was introduced by the Italian goldsmiths of the 13th century, and afterwards became popular in France. The design was generally worked in low relief, or chased on gold or silver, and brilliant translucent enamels were applied in such a way that the varying thickness produced differences of tint. This style is known as *basse-taille*. In certain rare enamels, probably of the 15th century, the pattern is outlined by strips of metal without any foundation, and the spaces in this grating are filled in with coloured transparent enamels ; such *cloisonné* work is termed *plique-à-jour*.

Artistic enamelling has been largely used, not only for inlaid and encrusted work, but for the production of paintings on metal. The painted enamels of Limoges, introduced in the 15th century, were usually executed on slightly convex plates of copper, the subjects being generally in white and grey on a deep-violet ground ; but the process was extended to the decoration of dishes, ewers, and other objects, and various colours were employed, sometimes heightened with gold. In this country, enamel painting was largely practised, by the family of Bone, during the latter part of the 18th and the early years of the following century. While their smaller works, or miniatures, were executed on gold, the larger examples were on plates of copper. The copper plate, having been annealed and cleaned with dilute sulphuric acid, was coated on both sides with white enamel powder ; it was then fired, and the enamelled face ground smooth. This white enamel, which was rendered so opaque by means of stannic oxide as to conceal the metal ground, was imported from Venice in the form of round cakes. The surface to be painted was further prepared by the application of a second coat of enamel, more fusible and transparent than the first ; this material, known to the enameller as 'flux,' was used in the form of rods and beads of white Venetian glass. Upon the fluxed surface, carefully ground smooth, the painting was executed in enamel colours, or powdered glasses mixed with an appropriate vehicle ; and as it was necessary to vitrify each colour separately, a complicated subject would require several successive firings in a muffle, each liable to injure or spoil the work. Recent years have witnessed a great revival in artistic enamelling, with the introduction of various improvements in technical details.

In addition to art enamels, there is a growing demand for coarse work in enamelled sheet-iron for street plates, railway notices, and other advertisements, which are generally executed in blue and white. In applying enamel to metal it is necessary to use a material which will adhere firmly to the base ; at the same time, it must fuse at a temperature lower than that which softens the metal, or melts the solder if any be present ; and the enamel should have a coefficient of expansion by heat as nearly as possible that of the metal ground. It is obviously important that, when enamel is used as a lining for saucepans, stew-pans, and other vessels for culinary purposes, it should be free from all ingredients which are poisonous, or may become so by contact with food. An important industry has been developed in recent years, especially in Germany, Austria-Hungary, and France, in the manufacture of vessels for domestic use, in cast or sheet metal ; soft sheet steel is commonly used for hollow ware.

The object to be enamelled, having been carefully cleaned by pickling in an acid bath, is coated with a thin layer of ground enamel. This primary coating need not be opaque, and generally contains a little cobalt or nickel oxide. A suitable material is obtained, according to P. Randau, by fusing a mixture of flint or quartz 30 parts, borax 25, and felspar 30. This product is then ground with kaolin 10·75 parts, felspar 6,

and magnesia, 1·25 ; the clay tends to lessen the fusibility. The finely powdered ground enamel is mixed with water to a creamy consistency and applied to the ware, slightly heated ; after the coating has dried, the object is fired in a muffle furnace at a temperature rather under 1000°. After this stage of enamelling, the ware is scrubbed to remove scale, and a second coating is applied, this time opaque white. This enamel may be made, according to the same authority, from a mixture of flint 37·5 parts, borax 27·5, tin dioxide 30, soda 15, nitre 10, ammonium carbonate 7·5, and magnesia 7 ; this mixture is fritted and then ground with flint 6·12 parts, tin dioxide 3·66, soda 0·7, and magnesia 0·7. The cover enamel is suspended in water and spread over the ground enamel, and the ware is then carefully fired in a muffle at a lower temperature than that of the first firing. In some cases a third coat of enamel is applied, while in other cases the ground layer is dispensed with, and only a single white coating used. Finally the surface may be decorated by painting or transfer printing in enamel colours, or by photographs. In some enamels, like 'granite ware,' the colour is applied by spraying.

(On enamels, v. Sir H. H. Cunynghame, On the Theory and Practice of Art Enamelling upon Metals, 3rd ed. London, 1906 ; Lewis F. Day, Enamelling, London, 1907 ; Alexander Fisher, The Art of Enamelling upon Metal, London, 1906 ; Philip Eyer, Die Eisenemaillierung, Leipsig, 1907 ; Paul Randau, Die Fabrikation des Emails und das Emailliercn, Vienna, 4th ed 1909 ; Enamels and Enamelling, English translation of P. Randau by Charles Salter, London, 1900 ; Julius Grunwald, translated by Herbert H. Hodgson, The Theory and Practice of Enamelling on Iron and Steel, London, 1909.)   F. W. R.

ENARGITE. Copper sulpharsenate Cu_3AsS_4 or $3Cu_2S\cdot As_2S_5$, occurring as orthorhombic crystals with perfect prismatic cleavages and usually a prismatic habit. The colour is iron-black with a metallic lustre ; sp.gr. 4·44. It is not a common mineral, but in a few copper-mining districts, for example, at Butte in Montana, Morococha in Peru, and in the Sierra de Famatina in Argentina, it is of some importance as an ore of copper.   L. J. S.

ENDIVE. *Cichorium endivia* (Linn.), the blanched leaves are used as a salad or garnish.

According to Konig, their average composition is—

				Other carbohydrates			
Water	Protein	Fat	Sugar	hydrates	Fibre	Ash	
94·1	1·8	0·1	0·8	1·8	0·6	0·8	

There are two chief varieties—with crinkled leaves and with smooth leaves. The former is apparently richer in nitrogen and ash, but poorer in carbohydrates (Dahlen, Landw. Jahrb. 1874, 3, 312, and 4, 614).

An analysis of the ash of endives by Richardson (Annalen, 67, 377) gave the following figures :—

| K_2O | Na_2O | CaO | MgO | SO_3 | P_2O_5 | SiO_2 | Fe_2O_3 |
| 37·9 | 12·1 | 12·0 | 1·8 | 5·2 | 3·0 | 24·6 | 3·4 |

H. I.

ENDLICHITE v. VANADIUM..

ENESOL v. SYNTHETIC DRUGS.

ENGLISH BROWN v. AZO COLOURING MATTERS.

ENGLISH GREEN, or CHROME GREEN, v. CHROMIUM ; PIGMENTS.

ENGLISH PINK, or ITALIAN PINK, v. PIGMENTS.

ENGLISH RED, or VENETIAN RED, v. PIGMENTS.

ENHYDROS v. AGATE.

ENSILAGE is a process of preserving green fodder for cattle. The term *silo* is applied to the pit or other depository in which the fodder (*silage*) is contained, and appears to be of Basque derivation, and originally meant a pit for storing grain. This method of preserving grass and other succulent forage crops has been in use for many years in Germany, whence the practice was carried to France, and afterwards to America. Although the German system had been fully described by Johnston, in 1843, in the Transaction of the Highland Agricultural Society (new series, 9), no general notice of it was taken in these islands until 1882, when a report of the British Legation at Washington on ensilage, as practised on Mr. Havemeyer's estate in New Jersey, was published as a blue-book, since which time many silos, of varying forms and construction, have been made in this country The object of all these is to exclude the air from the mass of fodder, allowing only a greater or less fermentation according to the practice of different authorities ; and to this end silos have been formed (1) wholly or partly underground ; (2) in the form of enclosed buildings. Silage has also been largely made by building up the green fodder in the form of an ordinary stack, of which only the top is covered. Whether it be silo or stack, the principal factor is the superposition of a sufficient pressure, either by dead weight or by some mechanical system of screws, levers, or similar appliances. The changes which forage undergoes in the silo are due to fermentation, and, as may be supposed, this action varies considerably with the materials stored and with the condition of storage ; as, for example, green maize undergoes principally lactic fermentation ; whilst in English fodder fermentation produces alcohol which is almost immediately converted into aldehyde. If the air has not been properly expelled from the silo, or if the fodder has been pitted in a very damp condition, the aldehyde becomes quickly converted into acetic acid.

Silage is of two kinds—viz. 'sweet' and 'sour.' Sweet silage is the result of allowing the grass to remain without pressure, and so permitting air to mingle with it until such time as a temperature of 125° to 150° F. is reached by the fermentation process ; sour silage, on the other hand, results when pressure is at once applied, whereupon an acetic or lactic fermentation takes place. It appears that a temperature of about 125° is sufficient to kill the bacteria which produce acid fermentation ; 'if the bacteria are killed and the silo is covered and weighted, the enclosed mass of green fodder will remain sweet, and be practically preserved under the same conditions as fruits, vegetables, or meats are preserved when canned. If this be the case, it will be at once intelligible that by less packing of the fodder when put into the silo, and extending the time of filling until the temperature rises to a point fatal to the bacteria, the resulting silage will be sweet and free from

acidity; whilst sour silage is produced by at once consolidating, covering up, and weighting the grass fodder so as to prevent the temperature rising to the point fatal to the bacteria (A. Voelcker, J. Roy. Agric. Soc. 20).

Two samples of sweet silage showed only a trace of acid, not exceeding in quantity that contained in ordinary fresh meadow grass :—

	Silage made from	
	Clover and rye grass mixed	Meadow grass
Moisture . . .	75·80	74·40
*Albuminoids . . .	2·53	2·56
Sugar and other carbohydrates soluble in water	1 43	2 99
Crude vegetable fibre .	18 31	17·90
Mineral matter (ash) .	1·93	2·15
	100·00	100·00
*Containing nitrogen .	0 40	0·41
Volatile acids (calculated as acetic acid) . . .	0 01	0 04
Non-volatile acids (calculated as lactic acid) . .	0 01	0·02

A sample of sour silage made from grass placed in a heavily weighted silo showed the following composition :—

Water . . .	76·01
Soluble albuminoids .	0 91
Insoluble albuminoids .	1·78
Soluble carbohydrates .	2 87
Crude fibre . .	15 82
Soluble mineral (ash) .	1·63
Insoluble mineral matter (ash)	0·98
	100 00
Total nitrogen . .	0·43
Volatile acids (calculated as acetic acid) . .	0 19
Non-volatile acids (calculated as lactic acid) . .	1·24

This silo was provided with a tap at the bottom from which juice was drawn off from time to time. This drainage had a sp.gr. of 1·022, and contained, per imperial gallon :

	Grains
Albuminoids . . .	1,008·56
Fixed acid (lactic acid) .	516·42
Volatile acids (butyric and acetic acids) . .	476·70
*Carbohydrates and amides	1,528·42
Mineral matters (ash) .	1,768·20
Water . . .	64,701·70
	70,000·00

*Containing non-albuminous nitrogen . . . 35·84

The dry matter (dried at 100°) which was left on evaporation of its drainage contained :

*Albuminoids . . .	20·90
Lactic acid . . .	10·71
†Carbohydrates and amides .	31·73
Mineral matter (ash) . .	36·66
	100·00

*Containing nitrogen . . 3·34
†Containing nitrogen . . 0 51

The subject of changes during ensilage has been very carefully investigated both at Rothamsted by Lawes and Gilbert, and at Woburn by Voelcker. The results obtained present a striking similarity, and it will suffice if one set of tables (those of Dr. Voelcker) is referred to here, although the Experiments on Ensilage conducted at Rothamsted (Lawes and Gilbert) should also be read. The silo to which these figures relate was one made at Woburn in 1886, and was of the character generally termed 'sour.' It was weighted with stones in strong elm boxes to 112 lbs. per square foot, and was unprovided with any drain. The silo was closed on July 3 and opened on December 16, the contents being 'very fair,' although 'not really fine,' meadow grass. The numbers, in a condensed form, are given in the following table.

QUALITY AND COMPOSITION OF THE GRASS PUT INTO SILO, AND OF THE SILAGE PRODUCED.

	Total weight	Water	Volatile acids	Non-volatile acids	Soluble albuminoids	Insoluble albuminoids	Digestible fibre	Woody fibre	Soluble carbohydrates, &c.	Soluble mineral matter	Insoluble mineral matter	Total nitrogen	Albuminoid nitrogen	Non-albuminoid nitrogen
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Grass put in silo	32,780	23,108	—	—	47	733	3278	2670	2265	430	249	151	123	28
Silage removed .	30,389	22,035	109	106	197	252	2326	2409	2254	471	230	155	73	82
Loss . . .	2,391	1,073	+109	+106	+150	481	952	261	11	+41	19	+4	50	+54
Loss per 100 lbs. of fresh grass .	7·29	3·27	+0·33	+0·32	+0·46	1·47	2·90	0·79	0·03	+0·12	0·06	+0·01	0·15	+0·16

The main features shown in the table are as follows : The total loss due to fermentation, evaporation, &c., in making the silage was 7·29 p.c. on the fresh grass. Of this, 3½ p.c. consisted of water, so that the loss in dry matter was only about 4 p.c. The loss of total nitrogen when, as here, no drainage was allowed to flow away is very slight ; but the nitrogenous bodies have undergone considerable change from the albu-minoid to the non-albuminoid condition, the fibre has been diminished, insoluble albuminoids have been lessened, and soluble albuminoids increased (Voelcker, J. Roy. Agric. Soc. 23, 410).

Since the nutritive value of food depends to a considerable extent on the albuminoid compounds contained in it, it becomes of importance from the economic point of view to determine the quantity of such compounds in fresh green

food and in silage. Kinch found that 55 p.c. of the total nitrogen present in the silage of grass was of a non-albuminoid nature, whilst in the original grass only 9 p.c. was of this form. In the case of mangold leaves, Kellner found that of the total nitrogen present, 27·8 p.c. in the original leaves, 45·5 p.c. in the silage, and as much as 59·7 p.c. in silage preserved in stoppered jars, was non-albuminoid. Clifford Richardson, examining maize silage, found :

	Per cent. total nitrogen as non-albuminoid
Original stalks . . .	21·2
Silage No. 1 . . .	44·6
„ No. 2 . . .	49·6
Dried fodder . . .	15·6
Silage from young maize .	53·3
„ „ older „ .	47·1

These results with grass, mangolds, and maize show that in ensilage a large portion of the albuminoids is converted into non-albuminoid nitrogenous substances, whilst in the ordinary drying of fodder no such change seems to take place. This is made clear by a reference to Dr. Voelcker's table given above under the heading ' Quality and composition,' &c., where the woody fibre, as indeed the whole of the fibre, has been diminished, insoluble albuminoids are lessened, and the soluble albuminoids increased.

Ensilage is largely practised in Canada and in America for the sake of having a supply of 'green' fodder during the winter months, especially in Canada where the winter is long. In England, since the interest attaching to novelty has waned, it has gradually died out of practice, except as a resource for adoption in unusually wet seasons, when haymaking is impossible or is so long delayed as to threaten loss of the crops. In such circumstances those who possess the simple tackle necessary for putting up silage stacks in the open field have a material advantage over their neighbours. Otherwise, in a country in which roots are easily grown and preserved for winter use, and where the actual period of the year in which vegetation is suspended is comparatively short, it would seem preferable, having regard to the deterioration which occurs in ensilage, especially as regards albuminoids, to adhere to the more ordinary practice of hay-making.

The application of silage as fodder and its practical effects with stock have been carefully investigated both at Rothamsted and Woburn.

(See Report on the Practice of Ensilage at Home and Abroad, Jenkins in J. Roy. Agric Soc., new series, 20 ; On the Chemistry of Ensilage, Voelcker, ibid. ; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1884–5 and 1885–6, Voelcker, ibid. 22 ; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1886–7, Voelcker, ibid. 23 ; articles in the Agricultural Gazette, April 27, 1855 et seq., by Sir J. B. Lawes and Sir Henry Gilbert, reprinted in pamphlet form under the title of Experiments on Ensilage conducted at Rothamsted.)

ENSTATITE. Metasilicate of magnesium, usually with some ferrous oxide isomorphously replacing magnesia, $(Mg,Fe)SiO_3$, and with increasing iron passing into bronzite and hypersthene. It belongs to the orthorhombic series of the pyroxene group, and is of importance as a rock-forming mineral and as a constituent of meteoric stones. Rarely it is clear and transparent and of a rich green colour, when it is used as a gem-stone ; such material is found in the ' blue ground ' of the South African diamond mines. L. J. S.

ENTEROL v. SYNTHETIC DRUGS.

ENZYMES and **ENZYME ACTION** v. FERMENTATION ; BARLEY ; CHEMICAL AFFINITY.

EOSAMINE v. AZO- COLOURING MATTERS.

EOSIN v. TRIPHENYL METHANE COLOURING MATTERS.

EOSOTE v. SYNTHETIC DRUGS.

EPHEDRINE, $C_{10}H_{15}ON$, crystals, m.p. 39°, b.p. 225°, occurs in Ephedra vulgaris. It is a secondary base, furnishes crystalline salts, and on ' exhaustive methylation ' yields eventually trimethylamine and a-phenylallyl alcohol $C_9H_{10}O$. On distillation the hydrochloride furnishes methylamine and propiophenone. When heated with hydrochloric acid, ephedrine undergoes isomerisation to ψ-ephedrine (isoephedrine), crystals, m.p. 117°, which also occurs with it in E. vulgaris. Both bases are poisonous and ephedrine hydrochloride has been used as a mydriatic (Ngai, Chem. Zentr. 1894, i. 470 ; Merck's Bericht, 1893, 13 ; Ladenburg and Oelschlägel, Ber. 1889, 22, 1823 ; Miller, Arch. Pharm. 1902, 240, 481 ; Flaecher, ibid. 1904, 242, 380 ; Schmidt and collaborators, ibid. 1905, 243, 73 ; 1906, 244, 239, 241, 269 ; 1908, 246, 210 ; 1909, 247, 141 ; 1911, 249, 305 ; 1913, 251, 320 ; Apoth. Zeit. 1911, No. 37 ; Fourneau, J. Pharm. Chim. 1904, [vi.] 20, 481 ; Emde, Arch. Pharm. 1907, 245, 662 ; Gadamer, ibid 1908, 246, 566 ; Calliess, Apoth. Zeit. 1910, 25, 677). According to Rabe (Ber. 1911, 44, 824) the ammonium base of ephedrine decomposes into water, trimethylamine and ɑ-phenylpropylene-αβ-oxide, and he regards ephedrine and ψ-ephedrine as optically isomeric β-methylamino-α-phenyl-propane-α-ols $OH·CHPh·CHMe·NHMe$ (cf. Emde, l.c.). This view is shared by Schmidt (Arch. Pharm. 1914, 252, 89 ; 1915, 253, 52), who considers the isomerism due to the difference in the spatial arrangement of the -- CHOH group. Cf. also Eberhard (Arch. Pharm. 1915, 253, 62). ɑ-Ephedrine has been synthesised by Nagai (Eng. Pat. 120936) and shown to differ from Fourneau's products and to be the racemic form of the natural variety (see Chem. Soc. Abst. 1919, i. 92).

The name ephedrine has also been applied by Spehr to a crystalline alkaloid $C_{13}H_{19}ON$, m.p. 112°, obtained from Ephedra monostachya, a drug used as a remedy for syphilis and gout in Bessarabia and Wallachia. Ordinary ephedrine is known commercially as ' ephedrine (Merck) ' and the second species as ' ephedrine (Spehr).'

EPICARIN,

$$HO·C_{10}H_6·CH_2 \diagdown \diagup OH \quad COOH$$
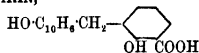
A derivative of β-naphthol used in the treatment of skin diseases. V. SYNTHETIC DRUGS.

EPICHLORHYDRINS a-epichlorhydrin (γ-chlorpropylene oxide) $CH_2·CH·CH_2Cl$ with an O bridge. Prepared by treating glycerol with phosphorus pentachloride or by heating the dichlorhydrins with

hydrochloric acid (Berthelot, Ann. Chim.&Phys. [3]·41, 299) ; by treating a- or β-dichlorhydrin with caustic potash (Reboul, Annalen, Spl. 1, 221 ; Tollens and Münder, Zeitsch. Chem. 1871, 252 ; D. R. P. 239077), or with alkali carbonates or alkaline earth hydroxides (D. R. P. 246242). Glycerol is treated with hydrogen chloride at 120°-130°, and the product distilled *in vacuó*. The fraction boiling at 50°-120°, which contains the dichlorhydrins, is treated with strong caustic potash solution, and the product distilled *in vacuó*. The portion boiling below 75° is washed with water and distilled. The fraction boiling at 118°-119° is crude epichlorhydrin, and may be purified by redistillation *in vacuó* (Fauconnier, Bull. Soc. chim. ii. 50, 212). Mobile liquid with odour resembling that of chloroform ; b.p. 116·6° (corr.) ; sp.gr. 1·2031 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 206) ; insoluble in water. With sodium in ethereal solution epichlorhydrin yields allyl alcohol and the diallyl ether of glycerol (Tornoi, Ber. 1888, 1209 ; Kijner, J. Russ. Phys. Chem. Soc. 24, 31) ; by heating with alkyl iodides, chloriodohydrin alkyl ethers are produced (Paal, Ber. 1888, 2971) ; ammonia gas converts it into trichlorhydroxypropylamine (Fauconnier, Compt rend. 107, 115) ; with potash in the presence of an alcohol, it yields the corresponding dialkyl ether of glycerol (Zunino, Atti. Real. Accad. Lincei, 1897, ii. 348 ; 1907, 9, i. 309) ; with phenols and sodium ethoxide, glyceryl diaryl ethers are formed ; whilst with sodium hydroxide, glycide aryl ethers are produced (Boyd and Marle, Chem. Soc. Trans. 1908, 838 ; 1909, 1803 ; Zunino, Atti. Real. Accad. Lincei, 18. i. 254 ; Cohn and Plohn, Ber. 1907, 2597 ; Lindemann, *ibid.* 1891, 2145) ; concentrated nitric acid oxidises it to β-chlorlactic acid ; alcoholic ammonia and ethylsodiomalonate convert it into chlorhydroxypropylmalonamide (Traube and Lehmann, Ber. 1899, 720) It combines with acid chlorides to form dichlorhydrin esters. Haller and March have synthesised ketolactonic acids and other unsaturated compounds by condensing epichlorhydrin with the sodium derivatives of benzoyl acetic esters of acetone dicarboxylic ester and of acetylacetone (Compt. rend. 132, 1459 ; 136, 434 ; 137, 11, 1203). It has also been condensed with aniline (Fauconnier, *ibid.* 106, 605 ; 107, 250) ; with p-toluidine (Cohn and Friedlander, Ber. 1904, 3037) ; with prussic acid (Lespieau, Compt. rend. 127, 965), and with salicylic acid (Lange, D. R. P. 184382 ; Chem. Soc. Abstr. 1906, i. 930). Organomagnesium compounds react with it to form substituted chlorhydrins of the type

$$R·CH{<}^{CH_2OH}_{CH_2Cl}$$
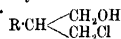
(Riedel, Chem. Zentr. 1907, i. 1607 ; D. R. P. 183361 ; Fourneau and Tiffeneau, Bull. Soc. chim. 1, [4] 1227). Epichlorhydrin has been used as a solvent for resins for photographic purposes (Phot. Korr. 1899, 2).

β-*Epichlorhydrin* (β - *chlorpropylene oxide*)

$$\overset{\text{—O—}}{CH_2·CHCl·CH_2}.$$ Obtained together with the a- compound and other products by treating the chloriodohydrins formed by treating allyl alcohol with iodine monochloride, with dry sodium hydroxide (Bigot, Ann. Chim. Phys. 22,

[6] 468). Liquid ; b.p. 132°-134°. Phosphorus pentachloride converts it into $\beta\gamma$-dichloropropylene, and sodium amalgam into allyl alcohol.

Polymerides. $(C_3H_5OCl)_2$. Obtained in the preparation of pyrazine bases by the distillation of glycerol with ammonium phosphate and ammonium chloride ; by treating the high-boiling fractions with hydrochloric acid, it is obtained crystalline ; m.p. 112°-113° ; b.p. 232°-233°. Readily soluble in hot alcohol, sparingly soluble in water.

$(C_3H_5OCl)_5$. Obtained by treating a-epichlorhydrin with hydrofluoric acid in a platinum dish. Yellow oil, soluble in alcohol, benzene, ether, or acetic acid. Dilute sulphuric acid at 200° converts it into a substance resembling cellulose (Paternò and Olivieri, Gazz. chim. ital. 24, i. 305 ; ii. 541).

Chlorbutylene oxide C_4H_7OCl. Obtained by treating a mixture of butenylglycerol and glacial acetic acid with hydrogen chloride ; b.p. 125·5° (corr.) at 738 mm. ; sp.gr. 1·098 at 15°/0 (Zikes, Monatsh. 6, 352).

EPIDIORITE. A rock consisting essentially of plagioclase-felspar and hornblende, and with a more or less marked schistose structure. It has been formed by the action of pressure-metamorphism on dolerite (*q.v.*), the augite of which has been thereby transformed into hornblende. Rocks of this class are of wide distribution, and being tough and hard they are much quarried for road-mending, for example, in Cornwall. Auriferous quartz-veins are often associated with epidiorites. L. J. S.

EPIDOTE. Basic silicate of calcium, aluminium, and ferric iron, $HCa_2(Al,Fe)_3Si_3O_{13}$, the alumina and ferric oxide replacing one another isomorphously, Fe_2O_3 ranging from 1·6 p.c. (in the clinozoisite variety) to 17 p c. The monoclinic crystals are usually much elongated in the direction perpendicular to the plane of symmetry, the habit thus being prismatic. The colour ranges from green to brown, and is usually a characteristic yellowish-green resembling that of a pistachio-nut, hence the name pistacite sometimes applied to this mineral. Sp gr. 3 3 –3·5 ; H. 6–7. Good crystals are found at many localities, and very fine ones at the Knappenwand in the Untersulzbachthal in Salzburg. These are of a deep green colour and are sometimes cut as gem-stones. Epidote is strongly pleochroic, and when manganese (Mn_2O_3) enters isomorphously into the composition this character becomes still more pronounced. This is seen in the withamite variety from Glencoe, Scotland, and in the cherry-red manganese-epidote (piedmontite) from San Marcel, Piedmont. As a rock-forming mineral epidote is abundant in crystalline schists and metamorphic rocks ; and it is often present in weathered igneous rocks. A rock composed of epidote and quartz is known as *epidosite* or epidote-schist, and sometimes carries gold. Banded epidosites have been used as ornamental stones. L. J. S.

EPINEPHRINE *v.* ADRENALINE ; also SYNTHETIC DRUGS.

EPININE. Trade name for 3.4-Dihydroxy-phenylethylmethylamine. *See* ADRENALINE.

EPIOSINE. Trade name for 1.methyl.4.5-diphenylene imidazole.

EPIRENAN *v.* SYNTHETIC DRUGS.

EPRONAL. Ethylpropylacetylurethane.

EPSOM SALTS. *Magnesium sulphate* (v. MAGNESIUM).

EPSOMITE or Epsom Salts, $MgSO_4,7H_2O$, as a mineral usually occurs as silky white fibres forming efflorescences in limestone caves, mine galleries, &c. Crystals are orthorhombic with spheroidal hemihedrism and a prismatic habit, the prism angle being nearly a right angle (89° 26′). Although good crystals are readily obtained by artificial means, in nature they are of rare occurrence. They have, however, been found in the salt deposits at Stassfurt in Prussia; where also a massive variety (' reichardtite ') ferms thin layers in carnallite. This epsomite is no doubt derived by the hydration of the more abundant kieserite, $MgSO_4,H_2O$. In Albany Co, Wyoming, and on the border of British Columbia and Washington, there are several small lakes containing rich deposits of compact white epsomite. At Epsom in Surrey, from which place the name is derived, the salt occurs only in solution in mineral waters

L. J. S.

ERBIUM or Neo-Erbium Sym. Er. At wt. 167·7. A dark-grey powder; sp.gr. 4·77 at 15° (S. Meyer, Monatsh 1899, 20, 793).

Sources.—Ytterbite (gadolinite), yttrotantalite, euxenite, xenotime.

The oxide of this metal belongs to the group of yttrium earths, forming with dysprosium and thulium the erbium sub-group, the salts of which are distinguished by their colour and by their characteristic absorption spectra in solution.

Separation and purification of the yttrium earths. The following methods have been employed in separating the closely related members of the yttrium earths :

1. *Fractional decomposition of nitrates* (Bahr and Bunsen, Annalen, 1866, 137, 1). The nitrates, heated until nitrous fumes are evolved, leave a vitreous residue of basic nitrates, the solutions of which, in hot water, slowly deposit, on cooling, small pink needles containing the greater proportion of the coloured erbium earths. The crystals are extracted with 3 p.c nitric acid, the solution evaporated, the residue again heated, and the whole series of operations repeated many times. The erbium earths accumulate in the less soluble basic salts, whilst the remaining yttrium earths, and any cerium earths which may be present, accumulate in the final mother liquors, and are not readily freed completely from the erbium earths. Further separation is effected by heating these nitrates from the final mother liquors so strongly that the residue consists of oxides mixed with insoluble basic nitrates. On extraction with water, the erbium compounds remain dissolved, and the operation is repeated till the more soluble yttrium salts no longer show absorption bands.

According to Wichers, Hopkins and Balke (J. Amer. Chem. Soc. 1918, 40, 1615) the nitrate fusion method is very efficient for separating erbium and yttrium and is much better than any of the later methods, although the cobalti-cyanide and the nitrite precipitation methods (v. supra) are both good, the latter being the more practicable and efficient.

2. *Differences in the solubility of the oxides.* —The oxides are mixed with water and treated

with an amount of nitric acid insufficient to convert the oxides into normal nitrates. The mixture becomes hot, and, after cooling, concentrated nitric acid is added until the product assumes a reddish tint. The precipitate is then digested with alcohol, which dissolves the normal nitrate, to the exclusion of the basic nitrates. The latter consists chiefly of erbium salts mixed with some ytterbium and scandium compounds, the more basic yttrium and cerite metals passing into solution. The final separation of erbium from ytterbium and scandium is effected by fractionally precipitating the basic nitrates by adding oxides to the solution of normal nitrates. In this operation ytterbium and scandium are precipitated as basic nitrates, while erbium remains dissolved (v. Drossbach, Ber. 1902, 35, 2826).

3. *Fractional precipitation by alkalis or aniline.*—The addition of ammonia to hot solutions of the salts of the yttrium group occasions the precipitation of basic salts which are easily filtered.

The neutral chloride dissolved in 50 p.c. alcohol is decomposed at 90° with alcoholic aniline, or the hydroxide is treated with aniline hydrochloride in aqueous solution (Drossbach, Ber 1896, 29, 2452 ; Mullmann and Baur, ibid. 1900, 33, 1748 ; 1902, 35, 2382 ; Urbain, Compt. rend. 1901, 132, 136 ; Kruss, Annalen, 1891, 265, 1 ; Zeitsch. anorg. Chem. 1893, 3, 108, 353, 407)

4. *Fractionation with ammonium carbonate and acetic acid* —The hydroxides of the yttrium group are moderately soluble in concentrated aqueous ammonium carbonate, and from this solution the earths may be fractionally precipitated by acetic acid (Dennis and Dales, J Amer. Chem. Soc 1902, 24, 400).

5. *Fractionation of oxalates, acetates, acetylacetonates, ethylsulphates* (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184 ; Marc, Ber. 1902, 35, 2370) ; formates (K. A. Hofmann, ibid. 1908, 41, 308), ferrocyanides (Bohm, Die Darstellung der seltenen Erden) ; bromates (James, J. Amer. Chem Soc. 1908, 30, 182) ; chromates (Kruss and Zoose, Zeitsch. anorg. Chem. 1893, 3, 92).

Various methods of separation of erbium from yttrium have been examined by Willand and James (J. Amer Chem. Soc. 1916, 38, 1198), who find that fractional precipitation with (1) sodium nitrite; (2) with potassium · cobalti-cyanide from a hydrochloric acid solution; (3) with sodium phosphate from a dilute nitric acid solution of the oxides on the whole yield the best results. In all three methods the last fraction was obtained by the addition of oxalic acid to the final liquors.

Erbia (*erbium oxide*) Er_2O_3. A pink powder obtained by heating the oxalate at 575°–845° ; sp.gr. 8·64 ; sp.ht. 0·065. So prepared is apt to retain carbon dioxide.

The salts of erbium have a pink or reddish colour, a sweet, astringent taste, and their solutions exhibit characteristic absorption bands in the red, green, and blue regions of the spectrum. The wave lengths corresponding with the two most prominent bands are as follows : λ 522·5–523·5 and 647·5–651·5.

Unless ionic dissociation is repressed, dilute solutions of the various erbium salts exhibit

identical absorption spectra (Zeitsch. physikal. Chem. 1906, 56, 624 ; v. Purvis, Proc. Camb. Phil. Soc. 1903, 12, 202, 206). The absorption bands undergo displacement when the solutions are placed in a magnetic field (J. Becquerel, Compt. rend. 1907, 145, 1412).

(For accounts of the flame, spark, and arc emission spectra, v. Thalén, ibid. 1880, 91, 326 ; Exner and Haschek, Wien. Akad. Ber. 1899, 108, IIa, 1071, 1123 ; • Eder, Chem. Zentr. 1916, i. 242 ; ibid. ii. 455.) . According to Eder erbium is probably complex.

Erbium salts exhibit signs of radio-activity (Strong, Amer. Chem. J. 1909, 42, 147).

Erbium sulphate $Er_2(SO_4)_3,8H_2O$. Pink monoclinic crystals, separating from aqueous solution at $20°$-$25°$; isomorphous with the corresponding yttrium, praseodymium, and neodymium salts (Kraus, Zeitsch. Cryst 1901, 34, 307).

The double sulphates $Er_2(SO_4)_3,K_2SO_4,4H_2O$ and $Er_2(SO_4)_3,(NH_4)_2SO_4,4H_2O$, are readily soluble in cold water.

Erbium nitrate $Er(NO_3)_3,5H_2O$. Large reddish crystals stable in air. When heated on platinum wire, the nitrate imparts an intense greenish colour to the flame, which, when viewed through the spectroscope, shows bright lines in the yellow-green and orange-blue regions of the spectrum. These bright lines correspond in position with the dark bands of the absorption spectrum.

Erbium formate $Er(CHO_2)_3,2H_2O$. Crystallises from cold aqueous solution.

Erbium oxalate $Er_2(C_2O_4)_3,10H_2O$ (K. A Hofmann, Ber. 1910, 43, 2631) is a reddish, sparingly soluble microcrystalline powder

Erbium platinocyanide $Er_2[Pt(CN)_4]_3,21H_2O$, like the corresponding yttrium salt, crystallises in red prisms with a green metallic reflex. For other salts, see Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10 ; Katz and James, ibid. 1913, 35, 872. G. T. M.

ERECTHIDIS OIL consists of a terpene $C_{10}H_{16}$, which boils at 175°, and at 18·5° has a sp.gr. of 0 838. This body absorbs a molecule of hydrochloric acid without the separation of a crystalline compound. The portion of the oil which boils above 200° also consists of a terpene (Beilstein and Wiegand, Ber. 15, 2854).

EREPSIN v. Enzymes, art. FERMENTATION.

ERGAMINE, ERGOSTEROL, ERGATHI-ONEÏNE, ERGOTIN, ERGOTININE, ERGO-TOXINE v. ERGOT.

ERGOT OF RYE. Spurred rye ; Ergota, B.P. ; U.S.P. Secale cornutum. (Ergot de seigle, Fr. ; Mutterkörn, Ger.) Ergot of rye consists of the dried sclerotium (resting stage) of the fungus Claviceps purpurea (Tulasne) developed from the ovary of the rye (Secale cereale). The grains are dark violet-black, 1–4 centimetres long, slightly curved and tapering at both ends. The same or a closely related fungus occurs on a number of other grasses, wild and cultivated, and on some Cyperaceæ. The first definite mention of ergot which the writer has been able to trace, is in the 1582 edition of Adam Lonicer's Kreuterbuch, cap. ccclxx. p. 285, where its use by midwives is also referred to. From an account by the medical faculty of Marburg, published in 1597, down to the middle of the

19th century, there is a voluminous literature in German and in French, on ergotism ; there seems little doubt, however, that the epidemic ignis sacer of the Middle Ages was also due to the presence of ergot in flour (cf. Ehlers, L'ergotisme, Paris, 1896). Only one outbreak of ergotism in England (due to wheat) has been described (Phil. Trans. Roy. Soc. 1762, 52, 530). The use of ergot by midwives was forbidden in several countries about 1770–1780, but in the second decade of the last century it was definitely introduced into scientific medicine by the American physicians Prescott and Stearns, and now ergot is only important as a drug, being chiefly employed as a stimulant of uterine muscle. In the United States ergot growing on wild grasses (especially on species of Elymus, cf. also Amberg, Schweiz. Woch. Chem. Pharm 1911, 49, 489), has occasionally given rise to extensive poisoning of horses and cattle. Further botanical and historical details are given by Fluckiger and Hanbury, p. 740. Cooke, Brit. Fungi, 772 ; Pharm J. [iii.] 1, 702 ; Parsons, Rep U.S. Commissioner Agriculture, 1880, 136 ; Holmes, Pharm. J. 1886, [iii.] 16, 684 ; Kobert, Historische Studien, Halle, 1889 ; Carruthers, Rep. Roy. Agric. Soc. 1874, [ii.] 10, 443 (with illustrations of ergot on other grasses).

The chief commercial varieties of ergot of rye come from Russia and from Spain. ' Bold ' ergot with large grains, is probably of no special value, because several writers agree that the larger grains have a smaller percentage of alkaloid than the smaller ones. Although they are not official, other ergots, growing on wild grasses, deserve attention as a source of alkaloid. E.g. that on Monilia cærulea has been found to contain as much as 0·81 p c. Festuca ergot contains 0·34 p c. (Pharm. J. 1913, 130). Perhaps ' Diss' ergot on Ampelodesmostenax (Link.), occurring along the coast of Algeria, might thus be utilised (cf. Germaix et Chassang, Rev. méd. et pharm. de l'Afrique du Nord, Alger, 1898, 1, 45, 78, 113, 146, 184 ; also Holmes, Pharm. J. 1886, [iii.] 16, 684). Diss ergot has better keeping properties than ergot of rye, about which the Brussels Conference agreed that it should not be more than one year old and should be preserved entire. The rapid deterioration of ergot seems to be due to oxidation, which is favoured by the presence of the oil. Hence removal of the latter by light petroleum has been recommended. Aymonier (J. Pharm. Chim. 1897, [vi.] 6, 359) suggests coating the ergot •with a dilute ethereal solution of tolu balsam.

The literature on the chemistry of ergot is as voluminous as that on ergotism. The first investigation is recorded by J. G. Model in his Chymische Nebenstunden (Wittenberg, 1771), seven years after von Münchhausen had first recognised the drug as a fungus. Among older writers we need, however, only mention here Tanret (Compt. rend. 1875, 81, 896), who first obtained the crystalline alkaloid ergotinine, and Buchheim (Arch. exp. Path. Pharm. 1874, 3, 1) who, albeit without experimental evidence, expressed the view that the activity of ergot is due to decomposition products of protein. The active principles of ergot have only been obtained pure in recent years. They

are a complex alkaloid and some simpler bases.

Ergotoxine $C_{35}H_{41}O_6N_5$, m.p. 162°-164°, an amorphous alkaloid yielding crystalline salts, of which the *phosphate* $C_{35}H_{41}O_6N_5.H_3PO_4H_2O$, m.p. 187°-188°, is the most readily obtainable (Barger and Carr, Chem. News, 1906, 94, 89; Trans. Chem. Soc. 1907, 91, 337; Barger and Ewins, *ibid.* 1910, 97, 284; 1918, 113, 235). This alkaloid had been obtained in an impure form as 'amorphous ergotinine' by Tanret, and was termed hydroergotinine by Kraft (Arch. Pharm. 1906, 244, 336; 1907, 245, 644), who, without analyses, first recognised it as a hydrate of Tanret's ergotinine.

The alkaloids of ergot are best obtained on a small scale by extracting the powdered drug with ether and shaking the ethereal solution with a weak acid (citric, tartaric). Excess of strongly ionised mineral acids precipitates the salts of the ergot alkaloids, which, on account of their high molecular weight, are semi-colloids. This property led many of the earlier investigators into error, but may be put to account when working on the large scale. The residue left on evaporation of an alcoholic tincture of ergot is extracted with light petroleum, to remove the fat. It is then dissolved in ethyl acetate and shaken with citric acid; sodium bromide solution then precipitates the mixed hydrobromides almost quantitatively. The latter are dissolved in dilute caustic soda, from which ether removes only ergotinine. The caustic soda solution is then neutralised, made alkaline with sodium carbonate and extracted again with ether. The crude ergotoxine left on evaporation, together with that from the mother liquors of the crystallisation of ergotinine (see below), is dissolved in 80 p.c. alcohol and a slight excess of syrupy phosphoric acid in alcohol is added. On standing for a few days the ergotoxine phosphate crystallises in thin needles, which on recrystallisation from 50 parts of 90 p.c. alcohol may be transformed into broad plates. They are soluble in 313 parts of cold and 14 parts of boiling 90 p.c. alcohol. By shaking with cold distilled water a 1 p.c. solution is obtainable, which is strongly opalescent and sets to a thick jelly on the addition of electrolytes. For physiological experiments ergotoxine is best dissolved in dilute sodium hydroxide.

Ergotinine, although not physiologically active, may be considered here. The alkaloid left on evaporation of its ethereal solution (above) readily crystallises from absolute alcohol in needles, m.p. 229° (corr.), and having the composition $C_{35}H_{39}O_5N_5$. It is extremely soluble in cold chloroform, and dissolves in 292 parts of absolute alcohol at 18°; in alcohol $[a]_D = +338°$; the solutions are strongly fluorescent. Prolonged boiling with alcohol lowers the rotation and produces an amorphous decomposition product. Heating in alcoholic solution with slightly more than one equivalent of (phosphoric) acid transforms ergotinine into ergotoxine phosphate which may be crystallised. The same change takes place slowly in cold dilute acetic acid. Conversely ergotoxine is dehydrated to ergotinine by boiling with methyl alcohol or by warming with acetic anhydride.

Both alkaloids give the following colour reaction (Tanret). A solution of 1 m.g. of the alkaloid in ether or in ethyl acetate is allowed to evaporate on the surface of concentrated sulphuric acid (containing oxides of nitrogen). A transitory orange colour is developed changing to violet-blue. Keller (Schweiz. Woch. Chem. Pharm. 1894, 32, 121) has improved this by dissolving 2-3 m.g. of the solid alkaloid in sulphuric acid on a watch glass and stirring in a trace of anhydrous ferric chloride, when an orange colour is produced, changing to deep red and then becoming blue or green at the edges. Alternatively the solution of the alkaloid in glacial acetic acid may be poured on sulphuric acid, without mixing. The test yields a positive result with the crude alkaloid from 1 gram of ergot.

Both alkaloids are sensitive to general alkaloidal precipitants, potassium mercuric iodide giving a faint opalescence with 1 part of alkaloid in 1-2 millions of water. On dry distillation both alkaloids yield a crystalline sublimate in *iso*butyryl formamide $CH(CH_3)_2CO\cdot CO\cdot NH_2$ (Barger and Ewins, *l.c.*). Ergotoxine probably contains a carboxyl group and ergotinine is the corresponding lactone. Both contain one N-methyl group, but no O-methyl group (Barger and Ewins, Chem. Soc. Trans. 1918, 113, 235). Ergotinine does not yield any crystalline salts.

The total alkaloids of ergot (*i.e.* ergotoxine + ergotinine) may be estimated by exhausting the finely powdered drug with light petroleum, mixing it with magnesia, extracting with ether and shaking the ether with dilute acid. After making alkaline with ammonia the alkaloids are again shaken into ether, and estimated gravimetrically (Keller, *l.c.*). For details and results of analysis, see Allen's Comm. Organic Analysis, 1913, vol. vii. p. 21. The alkaloidal content varies roughly from 0·1 to 0·4 p.c., and in Russian and Spanish ergot is generally between 0·2 and 0·3 p.c. König (Apot. Zeitsch. 1912, 27, 879) found 10 samples of German ergot to contain 0·032-0·14 p.c. An approximate idea of the ergotoxine content may be obtained by physiological means (Barger and Dale, Bio-Chem. J. 1907, 2, 240).

In addition to a specific alkaloid, the active principles of ergot comprise a number of simpler bases, derived from the amino-acids of protein by loss of carbon dioxide. Of these β-iminazolylethylamine (from histidine) and *p*-hydroxyphenylethylamine (from tyrosine) are therapeutically the most important. They can be prepared synthetically and are also formed by putrefaction. Their physiological action has been much studied of late and they have been applied practically.

Histamine (β-*iminazolylethylamine* 'β-1,' 4-β-*aminoethylglyoxaline, erganine*)

$$\begin{array}{c} CH=N \\ | \diagdown \\ NH\cdot CH \diagup \end{array} C\cdot CH_3\cdot CH_2\cdot NH_2$$
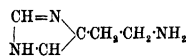
was obtained first synthetically by Windaus and Vogt (Ber. 1907, 70, 3691) and then by Ackermann (Zeitsch. physiol. Chem. 1910, 65, 504) by the putrefaction of histidine. Its intense physiological activity was not recognised until it was isolated from a commercial dialysed ergot preparation (Barger and Dale, Chem. Soc. Trans.

1910, 97, 2592). Kutscher (Zentralb. Physiol. 1910, 24, 163) isolated it simultaneously from ergot, but did not correctly identify it. The substance is certainly present in ergot as such, but its amount may be increased by such processes as prolonged extraction and dialysis. The base can be obtained directly from histidine by putrefaction (D. R. PP. 2528724, 256116, Hoffmann, La Roche & Co; D. R. P. 250110, F. Bayer & Co.; the yield is inconstant but may reach 60 p.c. or more). It may also be made from histidine by heating with acids (Ewins and Pyman, Trans. Chem. Soc. 1911, 99, 339; yield 25 p.c.). It is best obtained by reduction of the nitrile of iminazolylpropionic acid (Pyman, Trans. Chem. Soc. 1911, 99, 668), which nitrile in its turn is obtained most conveniently from histidine by the action of chloramine-T (Dakin, Biochem. J. 1916, 10, 322), although it may also be synthesised, according to Pyman (l.c.; cf. also Koessler and Hanke, J. Amer. Chem. Soc. 1918, 40, 1706). The most important salts are the phosphate $C_5H_9N_3\cdot 2H_3PO_4$ forming large crystals, and the d·picrate

$$C_6H_9N_3(C_6H_3O_7N_3)_2$$
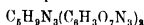
yellow rhombic leaflets, m.p. 238°–242° (corr.). The free base is readily soluble in water; its solutions give Pauly's histidine reaction with sodium p-diazobenzene sulphonate; a very distinct rose-pink colouration is still obtainable at 1 : 10,000.

Tyramine   (p-Hydroxyphenylethylamine) OH·C₆H₄·CH₂·CH₂NH₂ 'is similarly derived from tyrosine by loss of carbon dioxide. On a small scale it can be obtained by heating tyrosine to 260°–270° under reduced pressure (Schmitt and Nasse, Annalen, 1865, 133, 211; Ehrlich and Pistschimuka, Ber. 1912, 45, 1006, thus obtained a 50 p.c. yield). On a larger scale it is best got by reduction of p-hydroxy-benzylcyanide according to Barger (Trans. Chem. Soc. 1909, 95, 1123), who first isolated it from ergot. It also occurs as a product of putrefaction (Barger and Walpole, J. Physiol. 1909, 38, 343). The free base melts at 161° and boils at 175°–180° and 8 mm. It dissolves in 95 parts of water at 15° and can be extracted from aqueous solutions by shaking many times with ether, more readily by amyl alcohol. It gives Millon's reaction, the most characteristic derivative is the dibenzoyl compound C₂₂H₁₉O₃N, m.p. 170°·

Acetylcholine   .

OH(CH₃)₃N·CH₂·CH₂O·OC·CH₃
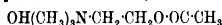
occurs in ergot and ergot extracts in varying small amounts. It was isolated by Ewins (Biochem. J. 1914, 8, 44) from a B.P. liquid extract. It is hydrolysed almost at once by rendering its solution alkaline with caustic soda.

Physiological action of the active principles.— Ergotinine is inert, but ergotoxine causes, on intravenous or intramuscular injection, a prolonged rise of blood pressure and contraction of the pregnant uterus. Repeated administration leads to dry gangrene, e.g. of the cock's comb, which is coloured purplish black by small doses, a reaction used at one time for the testing of ergot preparations (for criticism v. Cronyn and Henderson, J. Pharm. exp. Therap. 1909, 1, 231). Ergotoxine is the poisonous principle

responsible for epidemic ergotism (Kobert attributed the two types of this disease to the alkaloid cornutine and the resin sphacelinic acid, but both these substances seem to have been ergotoxine in an impure or modified form; cf. Barger and Dale, Biochem. J., 1907, 2, 240). β-Iminazolylethylamine is one of the most potent of drugs, causing marked contraction of the isolated guinea-pig's uterus in a bath containing 1 : 25,000,000. p-Hydroxyphenylethylamine resembles adrenaline in action, as in structure, but is much less potent; it causes a rather transitory rise of blood pressure. Acetylcholine is not a therapeutically desirable constituent It has a muscarine-like action, inhibiting the heart, and stimulates intestinal muscle (Hunt and Taveau, Hygienic Bulletin, Washington, No. 73, 1911). In most ergot preparations the amount is negligible. For a detailed account of the last three and most of the following bases, see Barger, the Simpler Natural Bases, Longmans, 1914.

In addition to β-iminazolylethylamine, p-hydroxyphenylethylamine and acetylcholine, there have been found in ergot quite a number of other substances of bio-chemical interest, which are not peculiar to the drug. They are inert, or have only a slight physiological action. Putrescine and Cadaverine (Rielander, Sitzber. Ges. Naturw. Marburg, No 7, 1908), isoamylamine (Barger and Dale, Proc. Physiol. Soc., May 15, 1909), and agmatine (Engeland and Kutscher, Zentralbl. Physiol. 1910, 24, 479) are all amines, derived respectively from ornithine, lysine, leucine and arginine, by decarboxylation. Agmatine has an action on the uterus like that of β-iminazolylethylamine, but very much feebler. It is guanidylbutylamine

$$NH_2\cdot C(NH)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2NH_2$$
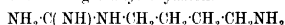
and was first discovered in herring roe by Kossel (Zeitsch physiol. Chem. 1910, 66, 257). A few amino-acids have also been found as such : leucine (Buchheim, l.c.), aspartic acid (Barger and Dale, Biochem. J. 1907, 2, 240), leucine, isoleucine, valine (van Slyke, J. Pharmac. exp. Therap. 1909, 1, 265). A mixture of these was described as an active principle, 'clavin' by Vahlen (Acrh. exp. Pharm. Path. 1906, 55, 131). There are further present choline which gives rise to the odour of trimethylamine, when ergot is treated with sodium hydroxide (Brieger, Zeitsch. physiol. Chem. 1887, 11, 184), (for acetylcholine, see above), betaine and uracil (Rielander, l.c.), vernine C₁₆H₂₀O₈N₈,3H₂O, which also occurs in leguminous seedlings (Schulze and Bosshard, Zeitsch. physiol. Chem. 1887, 10, 80), lactic acid, mannitol, trehalose, phytosterols and fats (see below).

Inert constituents which so far have not been found elsewhere are : secale aminosulphonic acid C₁₅H₂₆O₁₆(NH₂)SO₃H (Kraft, l.c.), prisms, m.p. 200°, soluble in water giving an acid solution ; ergothioneine C₉H₁₅O₃N₃S,2H₂O, isolated by Tanret (J. Pharm. Chim. 1909, [vi.] 30, 145) in an amount of 0·1 p.c. and shown by Barger and Ewins (Trans. Chem. Soc. 1911, 99, 2336) to be the trimethylbetaine of thiolhistidine; secalonic acid C₁₄H₁₄O₈, a crystalline yellow colouring matter, m.p. 244°, present to the extent of about 2 p.c. (Kraft, l.c.). This substance is probably the lactone of an hydroxy

acid, and possibly identical with sclerocrystallin (Dragendorff and Podwyssotzki, Arch. exp. Path. Pharm. 1877, 6, 174). Another crystalline yellow colouring matter $C_{15}H_{14}O_7,H_2O$, m.p. 350°, after regeneration of a crystalline acetyl derivative, has been described by Freeborn (Pharm. J. 1912, [iv.] 34, 568). The most important colouring matter of ergot, *sclererythrin*, is not known in a pure condition. It is the cause of the deep purplish red colour of the outer cells of the grain and is valuable for the recognition of ergot in flour, &c. The substance is acidic, and apparently present as a salt, for it is not extracted by ether until the ergot has been moistened with water containing tartaric acid. It is soluble in aqueous alkalis with a red colour. *Clavicepsin* $C_{18}H_{34}O_{16}$, m.p. 198° when anhydrous, $[\alpha]_D^{20} = +142\cdot27°$, was extracted from ergot by Marino-Zuco and Pasquero (Gazz. chim. ital. 1910, 41, 368). It is hydrolysed by acids to two molecules of glucose and one of mannitol. The *oil* is quantitatively the most important constituent (mostly 30–33 p.c.) and has been examined by Rathje (Arch. Pharm. 1908, 246, 692), who found D. = 0·9250, n_D = 1·4685 saponification number 179·3, acid number 11·38, iodine number 74·0, Hehner number 96·25, Reichert-Meissl number 0·63 and true acetyl number 27·44. The percentage composition is oleic acid 68, hydroxyoleic acid 22, palmitic acid 5, unsaponifiable matter 0·35, inorganic matter 0·2, alkaloid 0·6, and glycerol 7·5.

Ergosterol $C_{27}H_{42}O,H_2O$, m.p 165°, and *fungisterol* $C_{25}H_{40}O,H_2O$, m.p. 144°, have been separated by Tanret (Compt. rend. 1908, 147, 75). The second at least seems to exist in other fungi.

The detection of ergot in flour is based on the presence of alkaloids and of sclererythrin, and on the fact that the ergot particles float when the flour is shaken with an alcohol-chloroform mixture of density 1·435. After pouring off, alcohol is added, when the ergot sinks and can be examined microscopically. For further details, *see* Allen's Commercial Organic Analysis, vol. vii., 1913, p. 23, and Marino-Zuco and Duccini (Gazz. chim. ital. 1914, 44, 437).

For a critical discussion of the ergot preparations of the British Pharmacopœia, *see* Carr and Dale (Pharm. J. 1913, [iv.] 37, 130). It should be noted that 'ergotin' is not a pure substance, but a purified soft extract. The varying activity of different extracts should be controlled by physiological test. (G. B.)

ERGOTINE *v.* ERGOT OF RYE.

ERGOTININE *v.* ERGOT OF RYE.

ERICA B *v.* PRIMULINE.

ERICIN. Trade name for salicylic methoxy-

methyl ester $C_6H_4 {<}{\,}^{OH}_{CO\cdot O\cdot CH_2\cdot OCH_3}$

ERICOL. Guaiacol acetate.

ERICOLIN is found in several plants belonging to the order *Ericaceæ*, especially in the herb of the marsh wild rosemary, *Ledum palustœ* (Linn.) (Rochleder and Schwarz, Annalen, 84, 368), less abundantly in the common heath or ling, *Calluna vulgaris* (Salisb.) (Rochleder, *ibid.* €54), in *Rhododendron ferrugineum* (Linn.) (Schwarz, *ibid.* 361), and in the red bearberry, *Arctostaphylos Uva-ursi* (Spreng.) (Kawalier, Sitz. W. 9, 29).

To prepare it from *L. palustre*, the chopped leaves are thrown into boiling water and boiled for several hours. The filtrate obtained after adding basic lead acetate to the liquid is evaporated in a retort to one-third of its bulk. In Thal's modification of this process (Ber. 16, 1502), the liquid is concentrated *in vacuó*, the separated lead salt filtered off, and the liquid freed from lead by hydrogen sulphide. The filtrate is then evaporated to a syrup, and the ericolin dissolved out by anhydrous ether alcohol. The substance left on evaporating this solvent is repeatedly dissolved in a mixture of ether and alcohol till it no longer leaves any residue (Rochleder and Schwarz).

On heating the mother liquor obtained in the preparation of arbutin from the leaves of red bearberry with dilute hydrochloric or sulphuric acid, ericolin is deposited as a resinous precipitate, which may be purified by solution in alcohol and precipitation by water (Kawalier).

Rochleder and Schwarz, after deducting 10·6 p.c. ash, found ericolin to contain 51·71 p.c. carbon and 7·19 hydrogen, whence they deduced its formula to be $C_{34}H_{56}O_{31}$ (51·00 C and 7·00 H).

Thal (*l.c.*), after separating an admixed substance (containing 57·5 p.c. carbon and 7·29 hydrogen), which was insoluble in ether alcohol, from ericolin, assigned to the latter body the formula $C_{28}H_{24}O_3$, but subsequently altered it to $C_6H_{30}O_3$ to explain the decomposition equations of the substance. Ericolin, as prepared by Thal, is a brown-yellow, odourless, hygroscopic, bitter substance decomposing even below 100°. It is decomposed by water. By extracting successively with benzene, chloroform, and a mixture of ether and alcohol, different substances go into solution; it appears that the ericolin is thus broken up into a sugar and ericinol. With dilute sulphuric acid warmed to 100°, a sugar and a resinous brown-yellow viscid mass, hydroericinol, are produced. An analysis of the latter body gave numbers corresponding with the formula $x(C_6H_{12}O_2)$, subsequently modified to $x(C_5H_{10}O_2)$.

The equations representing these decompositions are as follows :—

$$C_{28}H_{30}O_3 + 4H_2O = C_6H_{12}O_6 + C_{22}H_{26}O$$
Ericolin.   Ericinol.

$$C_{22}H_{26}O + 7H_2O = 2(C_{10}H_{20}O_4)$$
Hydroericinol.
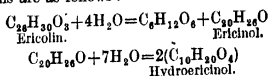
Power and Tutin, however, could not isolate ericolin by Thal's process, and they found that ericinol was identical with furfural (Chem. Zentr. 1907, i. 916).

Thal also isolated ericolin from *Calluna vulgaris* (Salisb.), and recognised it by the smell of ericinol in many *Ericaceæ* and *Vacciniea*.

Kanger extracted ericolin from the leaves of the cowberry (*Vaccinium vitis idœa*) by means of ether alcohol. It was then purified by precipitating foreign substances with lead acetate, and removing excess of the latter with sulphuretted hydrogen. The substance so obtained was of a resinous nature, completely soluble in ether alcohol, and corresponded with the composition $C_{16}H_{22}O_{10}$ (Chem. Zeit. 1903, 27, 794). Ericolin is probably not a chemical individual, but consists of a mixture of glucoside-like substances.

Ericolin is poisonous towards many microorganisms, particularly those belonging to the

colon group, but has no action on acid-fast bacilli. Twort (Proc. Roy. Soc. 1909, B. 81, 248) has used it as a medium for the isolation and culture of human tuberculous bacilli from sputum.

ERIGERON CANADENSE is an oil consisting of a terpene boiling at 176°, which, when pure, has sp.gr. 0·850–0·870, and an optical rotation +52°. It is soluble in an equal volume of alcohol, and rapidly resinifies.. The commercial oil has sp.gr. 0·8549–0·8963 ; optical rotation, +28° 48′ to 84·20° ; and b.p. 172°–178° (Kepler and Pancoast, Amer. J. Pharm. 75, 216).

According to Rabak (Pharm. Review, 1905, 23, 81 ; 1906, 326), the oil obtained from the fresh herb (0·66 p.c.) is of a bright-yellow colour with a peculiar odour like that of caraway. On exposure to air, it deposits crystals, and a brownish resinous mass is formed. The oil from the dried herb (0·26 p.c.) was darker in colour, had a powerful odour, and gave no crystals when exposed to air. It also differed from the fresh herb oil in sp gr., optical rotation. and other characteristics. In all probability, the terpeneol found in erigeron oil is a decomposition product. The oil absorbs two molecules of hydrochloric acid to form a solid dihydrochloride $C_{10}H_{16}$,2HCl, melting at 47°–48° (Beilstein and Wiegand, Ber. 15, 2854 ; Wallach, Annalen, 227, 292).

ERINOID. *See* GALALITH.

ERIOCOCCUS CORIACEUS. This is a scale insect consisting of a small pinkish-white sac occurring in clusters, and which encase the stems of young shoots of the Eucalypti, more especially those on old or burnt stumps. These insects contain a colouring matter which dyes wool mordanted with chromium, aluminium, tin, and iron, brown, light amber, pale orange-brown and sage-green shades respectively. The colours thus obtained are not specially brilliant, and are not fast to alkalis (Gurney, Report of the Australasian Association for the Advancement of Science, 1898).   A. G. P.

ERIOGLAUCINE. The trade name of the dyestuff obtained by condensing benzaldehyde-o-sulphonic acid with ethylbenzylanilinesulphonic acid (J. Soc. Chem. Ind. of Basle, Eng. Pat. 25128 ; Gnehm and Schüle, Annalen, 299, 347).

ERODIAMINE $C_{19}H_{17}ON_3$, light yellow plates, m.p. 287°, and *rutaecarpine* $C_{18}H_{13}ON_3$, light yellow needles, m.p. 258°, occur in the fruit of *Erodia rutaecarpa* (Asahina and Kashiwaki, J. Pharm. Soc. Japan, 1915, No. 405, 1293 ; Asahina and Mayeda, *ibid.* 1916, No. 416, 871 ; Amer. Chem. Soc. Abstr. 1916, 607 ; 1917, 332).

I. ·   II.
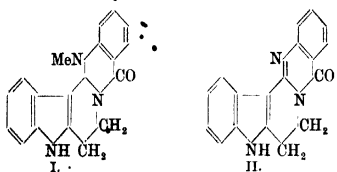
The annexed constitutional formulæ have been assigned. Perhaps they are not fully established, but they are of considerable interest as showing that the alkaloids are derivatives of

indole ; they also show a relationship to harmaline and harmine. On boiling with alcoholic hydrogen chloride erodiamine (I.) is converted into isoerodiamine $C_{19}H_{17}ON_3$,H_2O, m.p. 155°–156°, and this is decomposed by alcoholic potash into carbon dioxide, N-methylanthranilic acid and a base $C_{10}H_{12}N_2$, m.p. 120°, which has been identified as 2-β-aminoethyl indole. Isoerodiamine is regarded as

$$HN \cdot C_6H_4 \cdot CH : C \cdot CH_2 \cdot CH_2 \cdot N \cdot CO \cdot C_6H_4 \cdot N(Me) \cdot CHOH$$
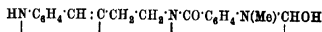
Rutaecarpine (II.) is similar to erodiamine, but more soluble in alcohol ; hot potassium hydroxide in ammonium hydroxide yields anthranilic acid, and an unidentified product, which on fusion with potassium hydroxide, like the base $C_{10}H_{12}N_2$ from erodiamine, yields 2-indole carboxylic acid   G. B.

ERUBESCITE *v.* BORNITE.

ERUCIC ACID $C_{22}H_{42}O_2$. A homologue of acrylic acid obtained, together with oleic acid, by the saponification of the fixed oil of white mustard. It was found together with behenic acid by Goldschmiedt (Sitz. W. 70, 451) in the oil expressed from black mustard, and by Fitz (Ber. 1871, 442) in the fat oil of grape seeds. It is best obtained by saponifying rape oil (from *Brassica campestris*, Linn.) with alcoholic potash distilling off the alcohol and dissolving the acid liberated on the addition of sulphuric acid in three times its volume of 95 p.c. alcohol ; on cooling to 0°, crystals of erucic acid separate out in an almost pure condition (Reimer and Will, Ber. 1886, 3320). It may be obtained by saponifying colza oil, freeing the erucic acid from arachidic acid by treatment with glacial acetic acid, in which the latter is insoluble (Ponzio, Gazz. chim. ital. 1904, ii. 50). It is also present in cod liver oil (Bull. Ber. 1906, 3570).

Erucic acid crystallises in colourless needles, m.p. 34° ; b.p. 281° at 30 mm. Heated with phosphorus oxychloride, it forms an anhydride $C_{44}H_{82}O_3$, an oil which may be crystallised in a freezing mixture. By treatment with nitrous acid, or better, by warming erucic acid with dilute nitric acid to the melting-point and then adding sodium nitrite, brassidic acid (brassic acid) is produced. This acid stands to erucic acid in the same relation as elaidic to oleic acid. *Cf.* Mascarelli, Atti R. Accad. Lincei, 1917, [v.] 26, i. 71. Fused with potash, erucic acid yields aradic (arachidic) and acetic acids. Concentrated nitric acid converts erucic acid into brassilic acid ($C_{13}H_{24}O_4$), pelargonic acid, arachidic acid, and a small .quantity of dinitrononane (Fileti and Ponzio, J. pr. Chem. [2] 48, 323), and concentrated sulphuric acid into behenolactone (Shukow and Schestakow, Chem. Zentr. 1908, ii. 1415). With hydriodic acid and amorphous phosphorus, it is converted into behenic acid (Goldschmiedt, J. 1876, 579). On treatment with phosphorus triiodide, iodobehenic acid is obtained, which on treatment with alcoholic potash, yields *iso*-erucic acid, m.p. 54° (Ponzio, *l.c.*). Erucic acid is converted into behenic acid by heating with iodine in a sealed tube for 4 hours at 270° (Reychler, Bull. Soc. chim. [3] 1, 296). When bromine is added to erucic acid under water, a dibromide $C_{22}H_{42}Br_2O_2$ is produced. It crystallises from alcohol in small white nodular crystals, m.p. 42°–43°, and is

reduced to erucic acid by sodium amalgam in alcoholic solution. Its barium and lead salts $(C_{22}H_{41}Br_2O_2)_2Ba$ and $(C_{22}H_{41}Br_2O_2)_2Pb$ are white, viscid, easily decomposable precipitates (Otto, Annalen, 127, 182; 135, 226). Erucic acid dibromide heated in sealed tubes to about 145° for 7–8 hours, with 4 or 5 mols. potassium hydroxide in alcoholic solution, yields the potassium salts of behenolic acid

$$C_{22}H_{40}O_2(=C_{22}H_{42}Br_2O_2-2HBr)$$

(Holt, Ber. 1892, 961). Behenolic acid, on treatment with zinc-dust and acetic acid, yields brassidic acid and not erucic acid. At ordinary temperatures, only 1 mol. of hydrobromic acid is abstracted by potash in alcoholic solution; monobromerucic acid $C_{22}H_{41}BrO_2$ is formed, with rise of temperature and separation of potassium bromide. On diluting the solution with water and adding hydrochloric acid, the acid separates as an oil which soon solidifies. It melts at 33°–34° and remains liquid for a long time. It is heavier than water, and insoluble therein, but dissolves readily in alcohol and ether. It unites with bromine, forming a dibromide $C_{22}H_{41}BrO_2\cdot Br_2$, which melts at 31°–32°, and forms amorphous viscid salts.

When erucic acid dibromide is triturated with water and an excess of silver oxide, and heated until it turns brown and evolves hydrogen bromide, the mass, on boiling with water, yields a yellow oil which is a mixture of liquid hydroxyerucic acid $C_{22}H_{42}O_3$ and dihydroxybehenic acid $C_{22}H_{44}O_4$. The latter partially crystallises out on long standing. For complete separation, the washed oil is saponified with baryta water; the precipitate is exhausted with ether and the dissolved barium hydroxyerucate is decomposed by hydrochloric acid. The hydroxyerucic acid, which separates as a colourless oil, is purified from alcohol. It is viscid, lighter than water, insoluble therein, but miscible in all proportions with alcohol and ether. Its salts $C_{22}H_{41}O_3M$ are amorphous. All excepting those of the alkali metals and barium are insoluble in water. Hydroxyerucic acid may also be formed from monobromerucic acid by the action of silver oxide. Boiled with potash lye, it is converted into dihydroxybehenic acid (Hausscknecht, Annalen, 163, 40). Dihydroxybehenic acid, m.p. 132°–133°, is also obtained by the oxidation of erucic acid with potassium permanganate (Hazura and Grüssner, Monatsh. 9, 947). Sodium erucate $C_{22}H_{41}NaO_2$ is soluble in alcohol, and gives precipitates of lead and barium erucates on the addition of an alcoholic solution of the acetates of these metals. The silver salt is a curdy precipitate, which becomes coloured on exposure to light.

Ethyl erucate $C_{22}H_{41}(C_2H_5)O_2$ is a colourless oil boiling above 360° without decomposition. The amide $C_{22}H_{41}O(NH_2)$, m.p. 84° (Reimer and Will, l.c.), m.p. 78°–79° (Krafft and Tritschier, Ber. 1900, 3580), and the anilide, m.p 55°, are crystalline bodies readily soluble in ether or benzene, sparingly soluble in alcohol.

ERUCIN. A crystalline body said to exist in white mustard seed. It is insoluble in water, sparingly soluble in alcohol, easily in ether or in oils (Simon, Pogg. Ann. 64, 293).

Dierucin $C_2H_4OH(C_2H_{41}O_2)_2$. When rape oil is allowed to stand for a long time, a yellowish tallow-like deposit is found frequently in the casks. This, by repeated solution in ether and subsequent addition of alcohol, may be obtained in silky needles. Dierucin melts at 47° and is readily soluble in ether and light petroleum, insoluble in cold but soluble in hot alcohol. A trierucin could not be separated from rape oil, but was obtained by heating dierucin and erucic acid at 300°, m.p. 31° (Reimer and Will, l.c.) (v. OILS AND FATS).

ERVASIN. Trade name for acetyl p-cresotinate.

ERYTHRENE. See BUTINENE.

ERYTHRIN, _Erythric acid, Erythrinic acid, Erythrolccanoric acid_ $C_{20}H_{22}O_{10},H_2O$, is a constituent of most lichens from which archil is prepared. It was discovered by Heeren (Schweigger's Jour. f. Chem. 59, 513) in _Rocella tinctoria_ (D. C.), from which lichen and several others of the same genus it may be extracted by boiling water, or better with milk of lime (cf. also Kane, Stenhouse, and Hesse (l.c.); Schunck, Annalen, 61, 69; De Luynes, Annales de Chim. [4] 2, 385; Menschutkin, Bull. Soc. chim. [2] 2, 424).

The method adopted by Stenhouse to prepare this substance from the _Rocella fuciformis_ is as follows (Annalen, 68, 72, and 149, 290). Three pounds of the lichen are macerated for 20 minutes in a milk of lime made by shaking ½ lb. of lime in 3 gallons of water, and the product filtered by means of a bag filter. The clear liquid, as it passes through, is immediately precipitated with hydrochloric acid, as prolonged contact with the lime decomposes part of the erythrin. The crude erythrin collected on bag filters is freed from acid and calcium chloride by stirring it up once or twice with a considerable quantity of water and again collecting.

Erythrin forms small colourless needles, melting at 148° (Hesse, Ber. 1904, 37, 4693), and not at 164°, as stated by Ronceray (Chem. Zentr. 1904, ii. 1504), and is sparingly soluble in water, easily soluble in alcohol, ether, and alkalis. Alcoholic ferric chloride gives a purple-violet colouration, which passes to brownish-red on addition of excess of the reagent.

When boiled with water, erythrin gives (a) orsellinic acid and (b) picro-erythrin (Schunck, Annalen, 61, 65)

$$C_{20}H_{22}O_{10}+H_2O=(a)\ C_8H_8O_4+(b)\ C_{12}H_{16}O_7$$
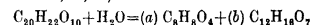
whereas by boiling with alcohol, picroerythrin and orsellinic acid ethyl ester (c) are produced (Heeren, l.c.; Kane, Annalen, 39, 25)

$$C_{20}H_{22}O_{10}+C_2H_5OH=(c)\ C_8H_7(C_2H_5)O_4+C_{12}H_{16}O_7$$
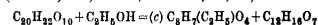
With amyl alcohol, a similar reaction occurs with formation of (d) amylorsellinate and picro-erythrin (Hesse, Annalen, 139, 22)

$$C_{20}H_{22}O_{10}+C_5H_{12}O=(d)\ C_8H_7O_4'C_5H_{11}+C_{12}H_{16}O_7$$
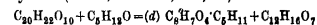
On the other hand, excess of lime water (Lamparter, Annalen, 134, 255) gives orcin, CO_2, and erythrite

$$C_{20}H_{22}O_{10}+2H_2O=2C_7H_8O_3+CO_2+C_4H_{10}O_4$$
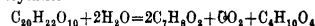
Tribromerythrin $2C_{20}H_{19}Br_3O_{10},3H_2O$ (Hesse, Annalen, 117, 310; and ibid. 139, 32) consists of white crystalline spherules which cake together a little above 100° and melt at 139°. Boiled with alcohol, it is resolved into _ethyldibromorsellinate_ and _brompicroerythrin_.

Picroerythrin or *erythro-orsellinic acid*

$$C_{12}H_{16}O_7,3H_2O$$
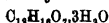
forms colourless prisms, melts at 158°, is readily soluble in hot water, and gives with ferric chloride a purple-violet colouration. It appears to be most readily obtained pure by Hesse's method of boiling erythrin with amyl alcohol (*l.c.*).

Digestion with hot baryta water converts picroerythrin into CO_2, orcin, and erythrite

$$C_{12}H_{16}O_7 + H_2O = CO_2 + C_7H_8O_2 + C_4H_{10}O_4$$
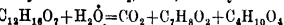
The experiments of de Luynes, Menschutkin, and Hesse have confirmed the view first put forward by Berthelot, that erythrin is the *mono-lecanoric ester* (1), and picroerythrin the *mono-orsellinic ester* of *erythrite* (2).

According to Hesse (Ber. 1904, 37, 4693), erythrin contains a free carboxyl group, and must therefore be represented as follows :—

$$C_4H_6(OH)_3 \cdot O \cdot C_6H_2(OH)CO \quad O \cdot C_6H_2(OH)COOH$$
$$\qquad \qquad \qquad | \qquad \qquad \qquad |$$
$$\qquad \qquad \qquad CH_3 \qquad \qquad \quad CH_3$$
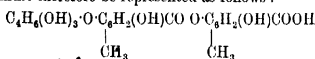
whereas picroerythrin has the formula .

$$O \cdot CH_2(CH \ OH)_2 \cdot CH_2OH$$
$$\qquad \quad |$$
$$\qquad \quad C_6H_2(OH)COOH$$
$$\qquad \quad |$$
$$\qquad \quad CH_3$$
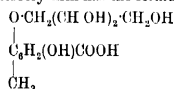
On the other hand, Zerner (Monatsch., 1914, 35, 1021) considers that the structure of erythrin is best represented thus :

Me   Me

HO $\langle$ $\rangle$—CO—O—$C_4H_6(OH)_2$—O—$\langle$ $\rangle$—COOH
      | |
      OH   OH
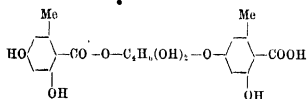
β-Erythrin $C_{21}H_{24}O_{10}$ is prepared by the action of lime water on some varieties of the *R. fuciformis* (Menschutkin, *l.c.*). It is a white crystalline powder ; m.p. 115°–116° (Lamparter, *l.c.*) ; nearly insoluble in water, soluble in alcohol and ether with violent evolution of CO_2. Boiled with water, orsellinic acid, and β-picroerythrin are produced ; with alcohol, the latter body together with ethylorsellinate.

β-Picroerythrin $C_{13}H_{16}O_{10}$ crystallises in needles, very soluble in water and alcohol. Boiled with baryta water, it is resolved into CO_2, erythrite, and β-orcinol (Menschutkin).

According to Hesse (*l.c.*), it is probable that β-erythrin is not a chemical individual, but consists mainly of erythrin, the properties of which are modified by the accompanying impurities. A. G. P.

ERYTHRITE or **Cobalt-bloom.** A mineral consisting of hydrated cobalt arsenate, $Co_3(AsO_4)_2$, $8H_2O$, crystallising in the monoclinic system and isomorphous with the iron salt vivianite. Sometimes, as at Schneeberg in Saxony, it occurs as beautiful radially-arranged groups of blade-shaped crystals with a bright crimson colour and brilliant lustre. More usually, however, it forms an earthy, peach-blossom red encrustation on other cobalt minerals, of which it is an alteration product. It has been found in the Dolcoath mine in Cornwall, Thuringia, Allemont in France, Cobalt in Ontario, Chile, &c The name was given by F. S. Beudant,

in 1832, from ἐρυθρός, red. The same name was also used by T. Thomson in 1843 for a flesh-red variety of orthoclase-felspar.

L. J. S.

ERYTHRITOL. *Erythrol, Erythromannite, Erythrite* (*v.* CARBOHYDRATES).

ERYTHRODEXTRIN *v.* DEXTRIN.

ERYTHROL NITRATE *v.* SYNTHETIC DRUGS.

ERYTHROPHLEINE $C_{29}H_{43}O_7N$ (?) is an amorphous alkaloid from Sassy bark of *Erythrophlœum guineense*, G. Don., a large leguminous tree from the West Coast of Africa. The bark is used as an arrow poison and in ordeals, and is also known as Casca, Red water, or Mancona bark. The alkaloid yields only amorphous salts, and is the only known one having a digitalis-like action on the heart. Heated with concentrated hydrochloric acid it is hydrolysed to methylamine and an amorphous acid. Erythrophlœine hydrochloride is used to a limited extent in medicine (Gallois and Hardy, Bull. Soc. chim. 1876, 26, 39; Harnack, Chem. Zentr. 1897, i. 301; Power and Salway, Amer. J. Pharm. 1912, 84, 337).

G. B.

ERYTHROSIN (*Tetraiodofluorescein*)

$$C_{20}H_8O_5I_4$$

is prepared by electrolysing a mixture of fluorescein (1 part) and finely powdered iodine (1·5 parts) in soda solution. The vessel is provided with a diaphragm, and the fluorescein mixture occupies the anode space, whilst a dilute solution of soda or sodium hydroxide forms the kathode liquid (D. R. P. 108838, 1899 ; Chem. Zentr. 1900, i. 1176 ; *cf. also* Frdl. 1877-87, 315).

The commercial product is a red-brick powder dissolving in dilute alkalis without any marked fluorescence. It can be purified by dissolving in aqueous ether, filtering and shaking with dilute sodium hydroxide. The sodium salt is precipitated by the addition of strong alkali, and, after filtering, washing, and recrystallisation from alcohol, it is dissolved in water, and the free erythrosin is liberated by treatment with hydrochloric acid (Mylius and Foerster, Ber. 1891, 24, 1482). When pure, it is of a lighter colour than the impure product, almost insoluble in absolute ether, benzene, or chloroform, but more readily so in acetone, alcohol, and aqueous ether. The colour of erythrosin fades under the influence of light and of hydrogen peroxide, particularly in the presence of potassium hydroxide (Zeitsch. Farbenindustr. 1908, 7, 299). Light also causes it to act hæmolytically in photodynamic reactions (Sacharow and Sachs, Chem. Zentr. 1905, i. 1420).

Erythrosin considerably enhances the action of light in its influence on bacteria (Mettler, Chem. Zentr. 1905, ii. 1037 ; Huber, *ibid.* 1906, i. 148 ; Sacharow and Sachs, *l.c.*). Erythrosin is employed in the cotton and paper industries ; and Thouert (Compt. rend. 1909, 148, 36) has attempted to apply it to colour photography, but with little success so far (*cf. also* Stark, Physikal. Zeitsch. 1907, 8, 248) ; it has also been used as a sensitiser in photo-electric experiments (Schlenderberg, J. Phys. Chem. 1908, 12, 574) and as an indicator in analysis (Mylius and Foerster, *l.c.* ; J. Amer. Chem. Soc. 1899, 21, 359).

Erythrosin is often mixed with rose Bengal (tetraiodochlorofluorescein) to suppress its fluorescence, and with common salt to increase its solubility. The former mixture is often used in France to colour foodstuffs, but the presence of rose Bengal in erythrosin is forbidden in America. Jean (J. Soc. Chem. Ind. 1908, 70) gives a method for testing and estimating rose Bengal in erythrosin.

Silver erythrosin, which is of an intense blue colour, is prepared by dissolving 1 gram of erythrosin in 400 c.c. water, adding 7·1 c.c. of a 10 p.c. solution of potassium bromide, and then 12 c.c. of a 10 p.c. silver nitrate solution. It forms a colloidal solution which becomes 'ripened' on warming or standing for a few days, depositing a very fine sediment which has a pure blue colour in transmitted light (Lüppo-Cramer, Zeitsch. Chem. Ind. Kolloide, 1907, i. 227 ; 1908, 2, 325).

The sodium or potassium salt is sometimes known as Erythrosin B, Pyrosin B, Iodeosin Dianthine B, Éosin J., &c.

ERYTHROXYANTHRAQUINONE $C_{14}H_8O_3$ is produced, along with an isomeric hydroxyanthraquinone, by the action of phthalic anhydride on phenol, in presence of sulphuric acid, $C_8H_4O_3 + C_6H_6O = H_2O + C_{14}H_8O_3$. Salicylic acid, anisole, and even anisic acid behave in the same way as phenol. The two hydroxyanthraquinones are separated by boiling with water and barium carbonate ; erythroxanthraquinone is unaltered by this treatment, whereas in the case of the isomeride a soluble barium compound is formed.

Erythroxanthraquinone may also be prepared from aminoanthraquinone, dissolved in acetic acid to which a little sulphuric acid has been added, by adding potassium nitrite till the solution becomes yellow. After a short time, on adding water and boiling, yellow flakes of erythroxanthraquinone separate, and increase as the acetic acid evaporates (D. R. P. 97688 ; Rower, Ber. 1882, 15, 1793 ; Perger, J. pr. Chem. [2] 18, 147).

It is also formed by oxidising the amino-salt with fuming sulphuric acid (D. R. P. 67063 ; Frdl. iii. 203) ; or by heating erythroxanthraquinone acid ($C_{15}H_8O_5$ at 270° (Birnkow, Ber. 1887, 20, 2438), and by heating anthraquinone-a-monosulphonic acid with a mixture of alkali hydroxide and a salt of an alkaline earth metal under pressure (Fr. Pat. 336867 ; J. Soc. Chem. Ind. 1904, 438 ; *ibid.* 1905, 841).

Erythroxanthraquinone crystallises from alcohol in groups of pomegranate-yellow needles, more soluble in hot than in cold alcohol. It melts at 173°-180° (Baeyer and Caro), at 190° (Liebermann), at 191° (Römer). It begins to sublime at 150°, and condenses to form fine needles, reddish-yellow in colour, like alizarin. It is almost insoluble in dilute ammonia, and only slightly soluble in strong ammonia. With lime or baryta water it gives a dark-red, almost insoluble lake, decomposable by carbon dioxide. The absorption spectrum of a sulphuric acid solution of erythroxanthraquinone differs from that of its isomeride, hydroxyanthraquinone; the latter body is also more easily converted into alizarin by fusion with caustic potash than the former (Baeyer and Caro, Ber. 7, 986).

Nitric acid oxidises ethythroxyanthraquinone to phthalic acid.

When sodium erythroxyanthraquinone sulphonate is heated with bromine and water at 120°-123°, 2 : 4-*dibromo*-1-*hydroxyanthraquinone* is formed, crystallising in reddish-yellow needles, m.p. 233°. When heated with p-toluidine at 80°-100°, this bromine derivative loses the bromine atom in the -4- position, and is converted into bromoquinizarin blue

$$C_6H_4 \underset{CO}{\overset{CO}{\diagdown}} C_6 \cdot HBr(OH)(NHC_7H_7)$$
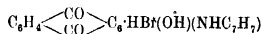
which crystallises in blue needles, giving a green colouration with sulphuric acid (D. R. P. 127532, 1902).

Erythroxyanthraquinone forms an acetate $C_{16}H_{10}O_4$, yellow needles, m.p. 176°-179° (Liebermann and Hagen, Ber. 1882, 5, 1804).

The constitution of erythroxyanthraquinone has been established by Liebermann (Ber. 10, 611 ; 11, 1611), who synthesised it from a reduction product of quinizarin, hydroxyhydroanthranol $C_6H_4 \underset{CH(OH)}{\overset{CH_2}{\diagdown}} C_8H_3(OH)$, in which the hydroxyl-group in the benzene nucleus occupies the ortho- position Frande (Ber. 12, 237) was also able to show that in methylhydroxyanthraquinone, a derivative of ordinary hydroxyanthraquinone, the hydroxyl-group was in the para- position, and hence, in the isomeric erythroxyanthraquinone, the hydroxyl- group must be in the ortho- position with regard to the ketone group. Erythroxyanthraquinone is therefore *o*-hydroxyanthraquinone (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

ESCALIN. Trade name for a paste of aluminium powder and glycerol.

ESERAMINE, ESERIDINE, ESEROLINE *v* ORDEAL BEAN.

ESERINE or **PHYSOSTIGMINE**

$$NHMe \cdot CO \cdot NHC_{13}H_{16}N \cdot OH$$

(Herzig and Meyer, Monatsh. 1897, 18, 389 ; Heubner, Chem. Zentr. 1905, ii. 1111 ; Straus, Ann. 1913, 401, 350 ; 1914, 406, 332 ; the most recent work is by Polonovski and callaborators, *e g.* van Bull Soc. chim. 1918, 23, 356) is the most important of the alkaloids occurring in Calabar bean, in the seed of which it was first found by Jobst and Hesse, in 1864 (Annalen, 1864, 129, 115 ; Hesse, *ibid.* 1867, 141, 82).

It is present in variable amount (0·04-0·27 p.c. Carr and Reynolds, Pharm. J. 1908, 542), and may be extracted by shaking the powdered seed with warm alcohol containing about 1 gram of tartaric acid per litre. The alcohol of the extract is distilled off and the residue is taken up with water, filtered to remove resinous matter and repeatedly shaken with ether until the latter ceases to be coloured. The aqueous extract is then made alkaline with sodium bicarbonate and finally repeatedly shaken out with ether. On evaporation, the alkaloid separates in scaly crystals which may be purified by recrystallisation from ether.

Eserine forms thin rhomboidal, colourless lamellæ, m.p. 105°-106°, which gradually assume a rose tint and even a yellow colour when exposed to air. It is sparingly soluble in water,

but readily so in alcohol, ether, chloroform, benzene, and carbon disulphide. Eserine is lævo-rotatory, its specific rotation varying between $-82°$ and $-120°$, depending on the solvent employed (Petit and Polonovski, Bull. Soc. chim. 1893, 9, 1008; cf. Orloff, Chem. Zentr. 1897, i. 1214). Polonovski and Nitzberg, Bull. Soc. chim. 1915, 17, 235 et seq.; idem. 1916, 19, 27, 46.

When eserine is isolated in the form of its salicylate, the base liberated with sodium carbonate, extracted with ether, and finally allowed to crystallise from a mixture of benzene and petroleum, it separates in stout prisms, m.p. $86°-87°$, $[a]_D$ $-75·8°$. By recrystallising in the presence of a crystal of Petit and Polonovski's modification, m.p. $105°-106°$, it is completely converted into the latter, and has $[a]_D-75·8°$; the alkaloid is therefore dimorphous (Salway, Chem. Soc. Trans. 1911, 2151).

When eserine or its salts are distilled with caustic potash in a current of hydrogen, methylamine and carbon dioxide are amongst the products of decomposition, whilst the residual liquid contains eseroline, a colourless crystalline body, which turns red by the action of moisture. Eseroline is also formed, together with methyl carbamide, when eserine is heated in a sealed tube with alcoholic ammonia at 150°. When heated with aqueous potash in presence of air, eserine yields rubreserine $C_{13}H_{16}N_2O_2$, red needles; these, in alkaline solution, are gradually converted into eserine blue, which, according to Ehrenberg (Chem. Zentr. 1894, ii. 439), is a true dye, colouring wool and silk without mordants. The constitution of eserine blue is not known, c.f. Salway, Chem. Soc. Trans. 1912, 986. It is not poisonous, but it has a paralysing effect on the heart and central nervous system of the frog (Heubner, l.c.).

Salts of eserine. Eserine salicylate

$$C_6H_4(OH)CO_2H,C_{15}H_{21}O_2N_3$$
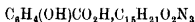
forms slightly bitter, colourless, stout prisms, m.p. $180°-181°$ (Salway), soluble in 150 parts of cold and 30 parts of boiling water, in which it forms an acid solution; it is more readily soluble in alcohol and in chloroform.

Eserine metacresotate (metahydroxytoluate)

$$C_{15}H_{21}O_2N_3·C_6H_3(OH)MeCO_2H$$
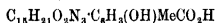
m.p. $156°-167°$, is prepared by mixing ethereal solutions of metacresotic acid and of eserine. Eserine benzoate, m.p. $115°-116°$, soluble in four parts of cold water, and eserine hydrogen citrate, are prepared similarly. The two former are not deliquescent, and yield neutral aqueous solutions; whereas the latter, and also normal eserine tartrate, prepared by dissolving eserine in tartaric acid and crystallising over sulphuric acid, are very deliquescent (Petit and Polonowsky, l.c.). The methiodide forms deliquescent yellow prisms, m.p. 100° (decomp.), and the sparingly soluble picrate crystallises in feathery yellow needles, m.p. 114°. Eserine yields no definite aurichloride or platinichloride.

Eserine sulphate $(C_{15}H_{21}O_2N_3)_2H_2SO_4$ is prepared by adding a 10 p.c. sulphuric acid, drop by drop, to an ethereal solution of eserine until the newly formed salt no longer separates. After filtration, it is carefully dried at about 40°. It

is a white or yellowish-white micro-crystalline powder, odourless, and having a bitter taste. It is readily soluble in water, alcohol, and in chloroform. Gold chloride solution, when added to the aqueous solution of the salt, gives a beautiful purple colour; whilst platinic chloride precipitates a yellowish-white salt. When evaporated with ammonia, the sulphate, like the salicylate, yields a bluish residue. If a little eserine sulphate is placed on a glass slip and moistened with water, and then a drop of sulphuric acid added, characteristic crystals of a sparingly soluble sulphate separate. This characteristic appearance is maintained for some time, but eventually the crystals become oily and then resinous (Reichard, Pharm. Zeit. 1909, 50, 375). Eserine and its salts turn red on treatment with alkali or on standing in solution, but the sulphite $C_{15}H_{21}O_2N_3,H_2SO_3$, the aqueous solution of which does not turn red, but remains colourless, has been prepared by Merck by treating a solution of eserine with sulphurous acid, and evaporating the mixture (D. R. P. 166310; J. Soc. Chem. Ind. 1906, 443). It is a white powder, readily soluble in water.

A derivative, the intensity of the fluorescence of which exceeds that of all known substances, is obtained by allowing an aqueous solution of physostigmine to stand for a few months until it has become deep blue, then adding phthalic acid. The substance forms dark-blue crystals with a blood-red fluorescence, and colours cotton, silk, alcohol, ether, &c., dark blue with no fluorescence. The aqueous solution, on the other hand, is colourless by transmitted light, but shows a beautiful red fluorescence by reflected light (Goubert, Compt. rend. 1909, 149, 852).

Eserine and its salts should be kept in amber-coloured, well-stoppered phials.

Test for eserine or its salts.—A small fragment (the size of a grain of sand) is placed in a porcelain capsule and dissolved in a drop or two of fuming nitric acid. The dark-yellow solution formed on warming is evaporated with stirring; the residue, which is of a pure green colour, dissolves in water, strong alcohol, and in sulphuric acid to a clear green solution. 0·005 gram of the alkaloid can thus be detected. The green colouring matter has been termed chloreserine (Ferreira da Silva, Compt. rend. 1893, 117, 330; Formanek, Chem. Zentr. 1895, i.1148; Reichard, l.c.). When exposed to nitric acid fumes, the blue residue becomes violet-blue; and when dissolved in a drop of nitric acid it forms a beautiful reddish-violet solution, which soon changes to blood-red, and on standing or on dilution becomes greenish-yellow. Eserine reduces molybdic acid very slowly in the cold, but rapidly gives a blue colouration on warming (Reichard, l.c.). With ammonium selenite in concentrated sulphuric acid, eserine gives a lemon-yellow colouration, which becomes orange, and then paler after standing for 3 hours (da Silva, Compt. rend. 1891, 112, 1266). Eserine can also be detected by means of the polarisation microscope (Kley, Rec. trav. chim. 1903, 22, 367). (For the estimation of eserine or physostigmine, see Heikel, Chem. Zentr. 1909, i. 949.)

Eserine and its salts are of considerable therapeutic value, being employed chiefly as a myotic to contract the pupil of the eye and to decrease intraocular pressure in glaucoma.

• According to Pal (Chem. Zentr. 1900, ii. 1031), eserine forms an antidote to the poisonous effect of curare.

Bilateral antagonism exists between eserine and curare in their effect on muscle. Those muscles which, like the diaphragm, are last paralysed by curare are first set free again by the injectio i of eserine. The latter also stimulates the respiratory centre (Rothberger, Pflüger's Archiv. 1901, 87, 117).

(For other investigations on the physiological effect and use of eserine or physostigmine, *see* Matthews and Brown, Amer. J. Physiol. 1904, 12, 173; Edmund and Roth, *ibid.* 1908, 23, 28, 46; Joseph, *ibid.* 1909, 23, 215; Anderson, J. Physiol. 1905, 33, 414; Magnus, Pfluger's Archiv. 1908, 123, 99; Kress, *ibid.* 1905, 109, 608; Modrakowski, *ibid.* 1907, 118, 52; Unger, *ibid.* 1907, 119, 373; Harnack, Chem. Zentr. 1908, ii. 338; Winterberg, *ibid.* i. 750; Loewi and Mansfeld, *ibid.* 1910, i. 941; Pewsner, Biochem. Zeitsch. 1907, 2, 339; Fühner, Arch expt. Path. Pharm., 1917, 82, 205) (*V.* ORDEAL BEAN.) G. B.

ESPARTO, *Stipa marcrochloa* (*tenacissima*) (Linn.). This grass is a native of Spain, Portugal, Greece, and North Africa. It is largely used as a raw material for paper making, having been introduced into this country by Routledge. For this purpose it possesses many advantages, as it grows abundantly without cultivation, is easily harvested, yields a large percentage of cellulose of high quality with comparatively simple treatment.

Of the various kinds known to commerce, such as Spanish, Tripoli, Arzen, Oran, Sfaz, Gabes, &c., the first-named is preferred by paper makers, as it yields more and better fibre. It therefore commands a higher price.

To give some idea of the importance of esparto as a paper-making material, it may be mentioned that the annual imports into the United Kingdom are between 200,000 and 300,000 tons.

It is also used for the purpose of making coarse mats and ropes (*v.* Spon's Enc. of the Industrial Arts).

Esparto arrives in this country firmly pressed into bales. The first operation which it undergoes in the paper mill is that of ' dry-picking,' in contradistinction to a subsequent process known as ' wet-picking.' The grass is spread out on tables covered with coarse wire cloth, and any root ends, weeds, &c., which may have found their way into the bales through imperfect gathering are picked out. Any sand or dirt escapes through the wire cloth. The removal of dirt can be more completely effected by machinery. For this purpose the grass is fed into a mechanical duster or willow, where it receives a violent shaking, the dirt being loosened and removed. The cleaned esparto is then fed into ' vomiting ' boilers, where it is treated with caustic soda solution at pressures varying from 10 to 40 lbs. per sq. inch for from 3 to 5 hours. The amount of soda required is about 17 lbs. of 60 p.c. caustic soda per cwt., but it varies with the quality of the grass, the form of boiler, the pressure at which it is boiled, and the time allowed. When the boiling is completed, the liquor is run away, evaporated to dryness, and ignited, and the alkali recovered in the form of

carbonate. This is dissolved in water, converted into caustic by means of lime, and is again available for use.

The boiled grass is washed once or twice in the boiler, and then subjected to the ' wet-picking ' process, whereby any unboiled portions are removed. The process is being gradually abandoned in favour of what is known as the ' presse-pâte ' system, which consists in purifying the pulp by passing it when bleached through a series of strainers and knotters. It is then made into a coarse web of pulp on the ' presse-pâte,' which may be described as a paper machine without the drying cylinders.

The subsequent treatment of esparto does not differ essentially from that of other fibres, and need not be particularly described.

The haulms (really leaves) of esparto vary in length from 0·3 to 0·5 m., the mean thickness being about 1·5 mm.; the individual fibres are 100–400 mm. long, and 0·009–0·5 mm. thick.

The fibres possess, owing to their fineness and their tendency to curl, considerable ' felting ' properties. Paper made from esparto is soft to the touch, ' bulks ' well, and at the same time is strong.

Esparto fibre can be recognised in a paper by the fact that when boiled with a solution of aniline sulphate a rose-pink colour is developed. A similar colour is produced with straw cellulose, but of a paler shade. With iodine and sulphuric acid the wall of the actual bast-fibre assumes a rusty colour, showing that it is not composed of cellulose ; with aniline sulphate (cold) it is stained yellow ; and with phloroglucinol and hydrochloric acid a crimson colour is assumed, thus demonstrating the presence of bodies characteristic of lignified walls. They can be distinguished by the size and shape of the peculiar serrated epidermal cells, which are to be seen when the commercial fibre is examined under the microscope.

Moreover, esparto pulp always has a number of the short conical, often hooked, hairs which line the inner (upper) surface of the ' rolled ' leaf, and which serve to distinguish it from straw ; the outer (lower) surface of the leaf is glabrous.

The chemical characteristics of esparto are those of the ligno-celluloses and the pecto-celluloses, the latter predominating.

Its composition is shown by the following analyses (Hugo Muller) :—

		Spanish.	African.
Cellulose	. .	48·25	45·80
Fat and wax .	.	2·07	2·62
Aqueous extract	.	10·19	9·81
Lignin and pectous			
substances	.	26·39	29·30
Ash . .	.	3·72	3·67
Water . .	.	9·38	8·80
		100·00	100·00

The names ' esparto,' ' sparto,' and ' alfa ' (' halfa '), are also given to the leaves of another grass, *Lygeum spartum* (Loefl.), which likewise grows in Spain and North Africa. These leaves are used as an inefficient substitute for those of *Stipa.* Microscopically they differ, in that the hairs have a considerable lumen, and are

usually blunt-ended; the epidermis has peculiar little rounded silica cells; and the ribs of bast fibres are isolated (not linked together to form a continuous band, as in *Stipa*).

ESTERIFICATION. The reaction between an acid and a monohydric alcohol appears, at first sight, to be exactly analogous to the neutralisation of an acid by a monoacid base: the equations are:

$$CH_3 \cdot CO \cdot OH + C_2H_5 \cdot OH = CH_3 \cdot CO \cdot OC_2H_5 + H_2O$$

and

$$CH_3 \cdot CO \cdot OH + NaOH = CH_3 \cdot COONa + H_2O$$
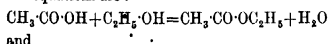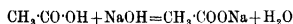
The product formed in the second reaction is a metallic salt, and that in the first reaction is termed an alkyl salt or more commonly an *ester*. The esters can be regarded as metallic salts in which the metallic radicals have become replaced by alkyl-groups. Corresponding with mono-, di-, and trivalent-metallic radicals are the mono-, di-, and trivalent hydrocarbon radicals, methyl CH_3-, ethyl C_2H_5-, propyl C_3H_7-, &c., methylene $CH_2=$, ethylidene $C_2H_4=$, &c., glyceryl $C_3H_5\equiv$, &c. The process of the conversion of an acid into its alkyl-salts is usually termed *esterification*, and is the common method by means of which esters are prepared. Although this reaction appears to be similar to the process of neutralising an acid by means of an alkali, there are two important points of difference.

1. The reaction between an acid and an alkali in aqueous solution is instantaneous, whereas the reaction between an acid and an alcohol is usually slow, and lends itself readily to study as a time reaction.

2. In the process of neutralisation between strong acids and strong alkalis, the reaction proceeds to completion when equivalent quantities of acid and alkali are used; but when equivalent amounts of acid and alcohol are brought together, complete conversion into ester and water never takes place. The reaction begins slowly and proceeds until a state of equilibrium is established. The rate at which the reaction proceeds, and the final equilibrium depend upon the specific acid and alcohol employed and upon the temperature. The process of esterification is a typical balanced or reversible reaction:

$$R \cdot CO_2H + R' \cdot OH \rightleftharpoons R \cdot CO_2R' + H_2O$$
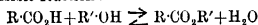
as the water formed in the process of esterification can hydrolyse the ester to a certain extent. This reaction is one of the best to study in order to illustrate the effects of mass action.

The reaction between acetic acid and ethyl alcohol was studied by Berthelot and Péan de St. Gilles, in 1862; they showed that working with equivalent quantities of alcohol and acid, equilibrium is reached when 66 p.c. of the reacting compounds have been transformed into ester and water. They were able to show that, by working with an excess of alcohol, a higher percentage of the acid can be transformed, as illustrated by the following numbers.

Equivalents of alcohol for 1 equivalent of acid	0·2	0·5	1·0	1·5	2·0	4·0	12	50
p.c. of acid transformed into ester	19	42	66·5	78	83	88	93	100

According to Guldberg and Waage's law of mass action formulated in 1867, the rate of chemical reaction is proportional to the concentrations (molecular) of the reacting substances, and to a constant which is characteristic of the reaction and retains the same value provided the temperature is constant. In the balanced reaction:

$$CH_3 \cdot CO_2H + EtOH \rightleftharpoons CH_3 \cdot CO_2Et + H_2O$$
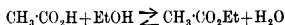
the direct reaction proceeds at a rate which can be denoted by $K.a.b$, where K is the specific constant for this reaction, and a and b are the concentrations of the acid and alcohol at the time of measuring the rate. Similarly, the reverse reaction proceeds at a rate $K'.c.d$, where c and d are the concentrations of the ester and water at the particular time. When the state of equilibrium is reached, we have:

$$K.a.b = K'.c.d$$

Using one equivalent of acid and one equivalent of alcohol, Berthelot and St. Gilles showed that equilibrium is reached when 0·66 mol. of acid and of alcohol have been transformed, leaving 0·33 mol. in the free state; we thus have:

$$K \times 0.33 \times 0.33 = K' \times 0.66 \times 0.66$$

$$\text{or } \frac{K}{K'} = \left[\frac{0.66}{0.33} \right]^2 = 4$$

The ratio K/K' is denoted by K, and is usually termed the equilibrium constant. It is the ratio of the constants for the direct and reverse reactions, and is independent of concentration, but may vary with temperature.

This equilibrium constant enables us to calculate the amount of acid transformed when any known quantities of the given acid and alcohol are mixed at the given temperature and kept until equilibrium is attained.

With a mixture of a, b, c, d equivalents of acid, alcohol, ester, and water at the given temperature, $a-x$ and $b-x$ equivalents of acid and alcohol will be present when equilibrium is attained, and $c+x$ and $d+x$ equivalents of ester and water will also be present, as each equivalent of acid reacts with an equivalent of alcohol and produces one equivalent of both ester and water.

$$\frac{K}{K'} = \frac{(c+x)(d+x)}{(a-x)(b-x)}; \text{ but } \frac{K}{K'} = 4$$

$$\therefore \frac{(c+x)(d+x)}{(a-x)(b-x)} = 4$$

and x can be calculated when a, b, c, d are known.

It is necessary to distinguish between esterification by means of the acid and alcohol alone, and esterification of an acid by an alcohol in the presence of a catalytic agent. The former process is generally termed 'direct esterification,' or sometimes 'autocatalytic esterification,' as it has been suggested that the organic acid itself can act as a catalyst to a certain extent. The second process is termed the catalytic method of esterification, and is the method most commonly used in the laboratory for the preparation of esters.

Catalytic esterification. The modern laboratory method is due to E. Fischer and Speier (Ber. 1895, 28, 3252). It consists in heating the acid with excess of alcohol, usually about five times the theoretical amount, in the presence of a catalyst. The most efficient catalysts are strong acids, and hydrogen chloride (about 3 p.c. of the alcohol) or concentrated sulphuric acid (about 10 p.c. of the alcohol) is generally used. When hydrogen chloride is used it is advisable to prepare a 3 p.c. solution of this in the alcohol before adding the organic acid. The 3 p.c. solution is best prepared by weighing the alcohol and passing in the dry gas by means of a delivery tube which just touches the surface of the liquid, and weighing from time to time until the requisite increase in weight is attained. The organic acid is then added, and the whole boiled in a reflux apparatus for 3 hours. The greater part of the alcohol is distilled off, the residue poured into about 5 times its volume of cold water, and the solution neutralised with sodium carbonate. It is then extracted with ether, the ethereal solution dried and distilled, when a 90 p.c. yield of the ester can usually be obtained. Esters which are readily hydrolysed by water, or esters which are extremely soluble in water, can sometimes be isolated by subjecting the reaction mixture to distillation under reduced pressure. J. and M. Phelps (Amer. J. Sci. 1907, [iv.] 24, 194) advise heating the acid, e.g. succinic or benzoic, with about its own weight of 1 p.c. alcoholic hydrogen chloride, and a small amount of solid zinc chloride at 100°–110°, and afterwards passing in a current of alcohol (compare *ibid.* 1908, 26, 281). For constants and properties of common esters, *see* Mathews and Faville (J. Physical Chem 1918, 22, 1.)

The function of the catalyst is to accelerate the rate of esterification; many acids which react very slowly with alcohol alone, e.g. acetic acid at the ordinary temperature, can be transformed rapidly into esters in the presence of a small amount of catalyst. Hydrogen chloride is a more efficient agent than sulphuric acid, the ratio being three to one (Kailan, Monatsh. 1909, 30, 21); but sulphuric acid is frequently used, as it is more convenient to work with. Phelps (Amer. J. Sci. 1908, [iv.] 260, 290, 296) has examined the action of various acid sulphates, e.g. NaHSO₄, KHSO₄, piperidine and aniline hydrogen sulphates, but finds that they are not so efficient as sulphuric acid, and similarly he has studied the action of metallic chlorides on the catalytic action of hydrogen chloride. Charcoal (Freundlich, Zeitsch. physikal. Chem. 1906, 57, 412) and finely divided platinum (Sudborough and Turner) also act as feeble catalysts. It is usually stated that the presence of the catalyst does not affect the equilibrium, and that provided the ratio of alcohol is kept the same, the percentage of ester formed when equilibrium has been obtained, is the same in both catalytic and direct processes; but Phelps does not agree with this statement. Ultra violet light brings about esterification of solutions of benzoic and other cyclic acids, especially in the presence of a trace of hydrochloric acid (Stoermer and Ladewig, Ber. 1914, 47, 1803).

The amount of ester formed by the catalytic process depends upon the specific acid and alcohol used, and tends to become less when the ester is readily hydrolysable. In the case of esters extremely soluble in water, or very readily hydrolysed, it is not advisable to pour into water, but to distil immediately under reduced pressure. Phelps and Eddy (Am. J. Sci. 1908, 26, 253) recommend adding solid potassium carbonate to the reaction mixture and distilling under reduced pressure. Certain finely divided metallic oxides have a catalytic action on the formation of esters.

A method of catalytic esterification consists in passing a mixture of the vapours of the acid and alcohol through a tube containing finely divided titanium dioxide at 290°–300° (Sabatier and Maihle, Compt. rend. 1911, 152, 494 ; A. Mailhe, Chem. Zeit. 1913, 37, 777 and 806).

According to Hauser and Klotz (Chem. Zeit. 1913, 37, 146), glucinum oxide is more efficient than titanium oxide, and even tertiary alcohols yield esters when this oxide is used.

Senderens and Aboulenc (Compt. rend. 1911, 152, 1671, 1855 ; 1912, 155, 168, 1012) state that by the addition of 5 p.c. of aluminium sulphate or of potassium hydrogen sulphate to a mixture of equivalent amounts of acetic acid and ethyl alcohol an 82 p.c. yield of ester is obtained, and that 1 p.c of sulphuric acid by volume gives an 86·5 p.c yield. The actual catalyst is stated to be ethyl hydrogen sulphate.

Various esters derived from cyclic alcohols, e.g. cyclohexanol, have been prepared by the method. The temperature, however, must not be too high and the method does not work with aromatic acids containing a carboxylic group directly attached to the benzene nucleus.

For use of (a) anhydrous calcium chloride, *see* Chem. Soc. Abstr 1911, i. 601, (b) nickel sulphate Kurtenacker and Habermann, J. Pr. Chem. 1911, (ii.) 83, 541, and (c) dilute sulphuric acid Bodroux, Compt. rend. 1913, 156, 1079 ; 157, 938, 1428. A convenient method for certain esters appears to be a saturated aqueous solution of sodium chloride as solvent and a little sulphuric acid as catalyst.

Relationship between constitution and esterification using the catalytic method. V. Meyer and Sudborough (Ber. 1894, 27, 510, 1580, 3146) were the first to point out any clear relationship between the constitution of an acid and its conversion into an ester by the catalytic method. Their original method was to saturate the alcoholic solution of the acid with hydrogen chloride, to leave at the ordinary temperature for several hours, and then to isolate and weigh the ester formed. Subsequently the Fischer-Speier method was used. They were able to show that practically any substituted benzoic acid, in which the two ortho- positions with respect to the carboxylic group are substituted, does not yield appreciable amounts of ester when its alcoholic solution is saturated with hydrogen chloride and kept for several hours at the ordinary temperature, or when the acid is boiled with a 4 p.c. solution of hydrogen chloride in alcohol. All substituents react in much the same manner, e.g. CH₃, Cl, Br, F, I, CO₂H, NO₂, &c., but the substituents F, OH, CH₂ have not so marked an effect as nitro-, carboxylic, and halide radicals ; e.g. acids of the type

$$C_6H_2Me_3 \cdot CO_2H(CO_2H : Me_2 = 1 : 2 : 4 : 6)$$

are esterified to an appreciable extent when hydrogen chloride is passed through their

boiling alcoholic solutions for several hours (Meyer and Sudborough, Ber. 1894, 27, 1580; Meyer, *ibid.* 1895, 28, 182, 1254; compare also Kahn, *ibid.* 1902, 35, 3857).

The presence of a second benzene nucleus, as in naphthalene- and anthracene-carboxylic acids, has much the same effect as nitro- or halogen substituents; thus 2-chloro-1-naphthoic acid, anthracene-7-carboxylic acid and 1-chloroanthracene-9-carboxylic acid do not yield esters by the catalytic method, whereas the isomeric 3-chloro-2-naphthoic acid, anthracene-1-carboxylic acid, and 3-chloroanthracene-2-carboxylic acid yield 90 p.c. of ester under the same conditions.

It has been shown by V. Meyer (Ber. 1895, 28, 3197; and Rupp, *ibid.* 1896, 29, 1625) that the dibasic acids :—tetrachloro-, tetrabromo-, and tetraiodo-terephthalic acids, tetrachloro-, tetrabromo-, and tetraiodo-*iso*phthalic acids, *i.e.* acids in which both carboxylic groups are diortho- substituted, do not yield esters when heated with a 3 p.c. solution of hydrogen chloride in alcohol. An acid in which one of the carboxylic groups is diortho- substituted and the other is not, yields an acid ester under similar conditions, *e.g.* 2 : 6-dimethylterephthalic

acid, $C_6H_2Me_2(CO_2H)_2$ gives CO_2Me

(Jannash and Weiler, Ber. 1895, 28, 531). Similarly, hemipinic acid, 3:4-dimethoxyphthalic

acid, gives the acid ester

(Wegscheider, Monatsh. 1895, 16, 135). (For further examples, *see* Wegscheider, *ibid.* 1900, 21, 621, 638; 1902, 23, 405; McKenzie, Chem. Soc. Trans. 1901, 79, 1135.) An apparent exception is met with in the case of 3:6-dichlorophthalic acid, which, according to Graebe (Ber. 1900, 33, 2026), yields the acid ester

when its alcoholic solution is saturated with hydrogen chloride and kept at the ordinary temperature. Tetrachloro-, tetrabromo-, and tetraiodo-phthalic acids also yield acid esters (Rupp, *ibid.* 1896, 29, 1625); o-nitrophthalic acid and papaverinic acid (Miller, Annalen, 1881, 208, 243; Wegscheider and Lipschitz, Monatsh. 1906, 21, 790; Wegscheider, *ibid.* 1902, 23, 369) behave in a similar manner, yielding neutral esters, and it is probable that the esters are formed by the conversion of the acids into their anhydrides under the influence of the hydrogen chloride or sulphuric acid, and the subsequent addition of alcohol to the anhydrides. 3:6-Dichlorobenzoylbenzoic acid and tetrachlorobenzoylbenzoic acid are also readily esterified, and it is possible that these react with alcohol as the tautomeric hydroxyphthalides; *e.g.* :
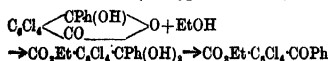
(Graebe). The results obtained with tri-, or even hexa-carboxylic acids show the same inhibiting effect of ortho-substituents. Thus trimesic acid, benzene 1:3:5-tricarboxylic acid, yields a neutral ester; hemimellitic acid, the 1:2:3-tricarboxylic acid, yields a dimethyl ester; pyromellitic acid, benzene-1:2:4:5-tetracarboxylic acid, yields a normal ester; prehnitic acid, 1:2:3:4-tetracarboxylic acid, gives a dimethyl ester in the cold, and the neutral ester on heating; the formation of the latter is probably due to the fact that an anhydride is first formed, and this, with methyl alcohol, gives the dimethyl ester
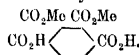
which is further esterified to the normal ester. Dinitro-pyromellitic acid, mellitic acid, and hexahydromellitic acid do not yield esters (Meyer, Ber. 1894, 27, 1590; 28, 182; 1896, 29, 840). *Iso*hydromellitic acid, on the other hand, yields a monomethyl ester (Van Loon, *ibid.* 1895, 28, 1272).

Substituted benzoic acids in which the substituents are not in ortho- positions, give good yields of esters by the Fischer-Speier method, and this difference in behaviour has been used for the following purposes : 1. Separation of an ortho-disubstituted benzoic acid from isomerides (compare Martz, Ber. 27, 3147, for separation of dinitro-benzoic acids; Jannasch and Weiler, *ibid.* 3445, for separation of isomeric trimethyl-benzoic acids). Rosanoff and Prager (J. Amer. Chem. Soc. 1908, 30, 1912) show that a mixture of benzoic acid with an ortho- substituted benzoic acid can be separated by partial esterification in the cold with a 3 p.c. solution of hydrogen chloride in ethyl alcohol. 2. Determination of the constitution of particular substituted benzoic acids. (Compare V. Meyer, Ber. 1895, 28, 187, for 2-methyl-5-bromobenzoic acid; Zincke and Francke, Annalen, 1896, 293, 123, for 4-acetyl-5-bromo-*iso*-phthalic acid; and Matthews, Chem. Soc. Proc. 1900, 16, 187, for 2:3:5-trichlorobenzoic acid. *See* also Blaise, Compt. rend. 1898, 126, 733, for substituted succinic acids.)

When the carboxylic group is not directly attached to the benzene nucleus, but is united to a side chain, the presence of ortho- substituents does not prevent the formation of esters, *e.g.* 2:4:6-tribromo-3-aminophenylpropionic acid and 2:4:6-tribromophenylpropionic acid, mesitylacetic and mesitylglyoxylic acid all gave good yields of esters when the alcoholic solutions are saturated with hydrogen chloride. Kellas (Zeitsch. physikal. Chem. 1897, 24, 221) and Goldschmidt (Zeitsch. lect. Chem. 1909, 15, 4) have shown that the introduction of one ortho- substituent into the benzoic acid molecule retards esterification to an appreciable extent, the nitro- group having a greater inhibiting effect than Me, Cl, Br, or I. Kailan also shows that o-aminobenzoic acid hydrochloride is esterified more slowly than its isomerides (Monatsh. 1906, 27, 1038); but he finds that o-nitrocinnamic acid is esterified more readily than the p- and m-nitro acids (*ibid.* 1907, 28, 1163). Goldschmidt was able to show that using a dilute alcoholic solution of the acid with hydrogen chloride as catalyst, the velocity of the reaction can be determined by means of the equation for a unimolecular reaction, $K=$

$1/t(\log a/a-x)$; since under these conditions the mass of the alcohol can be regarded as constant, and the reaction is practically non-reversible in the presence of the large excess of alcohol. The concentration of the acid at any given moment can be determined by direct titration with standard barium hydroxide solution, using phenolphthalein as indicator. When, however, the ester formed is readily hydrolysed, as in the case of ethyl formate, ethyl trichloracetate, and ethyl pyruvate, it is necessary to titrate with ammonium hydroxide solution, using litmus as indicator, as the end point is not definite when baryta is used, owing to the instantaneous hydrolysis of the ester by the baryta. The constant K is directly proportional to the concentration of the hydrogen chloride in the absence of water, and falls somewhat as t (time) increases, owing to the fact that the water produced during the esterification has a retarding effect. The influence of small amounts of water has been studied by Kailan (Monatsh. 1906, 27, 543, 997 ; 1907, 28, 115, 571, 673, 705, 965, 1069, 1137, 1187 ; 1908, 29, 799 ; 1909, 30, 1), who has shown that the relationship between the rate of esterification and the amount of water can be represented by means of an equation of the type, e.g. in the case of cinnamic acid

$$\frac{1}{K}=0.665+\frac{4876}{c}-\frac{1.678}{c_2}+\left(2.911-\frac{3.212}{c}+\frac{4.358}{c_2}\right)w$$
$$+\left(-27.54+\frac{31.78}{c}-\frac{2.284}{c_2}\right)w^2$$

for concentrations of water $w=0.3$ to 1.3, and for concentrations of hydrogen chloride $c=0.15$ to 0.66. (Compare also Fitzgerald and Lapworth, Chem. Soc. Trans. 1908, 93, 2168.)

The inhibiting action of water on a mixture of acid and alcohol is readily shown by comparing the rates of esterification of the same mixture of acid and alcohol : (a) in presence of water ; (b) in presence of a corresponding quantity of benzene (Kailan, Zeitsch. physikal. Chem. 1915, 89, 676). When 25 or 50 volume p.c. of alcohol is used the relative effects of benzene and water are as 1 : 100 or 150. The effect of water on the esterification of dibasic acids has also been examined (Kailan, ibid. 1913, 85, 706 ; 1914, 87, 619).

Sirks (Rec. trav. chim. 1908, 27, 237) has obtained the following values for the esterification constants of the isomeric dinitrobenzoic acids at 25°, using ethyl alcohol containing a little water with hydrogen chloride as catalyst : 3 : 4-dinitro-acid, 0.0086 ; 3 : 5-acid, 0.0050 ; 2 : 3-acid, 0.0005 ; 2 : 5-acid, 0.0003 ; 2 : 4-acid, 0.0002 ; and 2 : 6-acid, nil. The values for $E_{EtOH}^{25°}$ obtained for benzoic, m-, and o-nitrobenzoic acids were 0.0132, 0.0071, 0.001.[1]

These numbers indicate the retarding effect of one or two nitro- groups in the ortho- position ; even one m- group retards, but the introduction of a second nitro- group into the meta- position of the m-nitro- acid molecule, increases the rate.

[1] The letter E is used to denote the esterification constant of an acid, using normal hydrogen chloride as catalyst, and the temperature and specific alcohol are also given, as the constant varies with these.

From a comparison of the rates of esterification of these acids with their dissociation constants, Sirks comes to the conclusion that acids with small dissociation constants are esterified more readily by the catalytic method than acids with high dissociation constants ; but an examination of certain alkyl- derivatives of aliphatic acids shows that the statement does not hold good generally.

Sudborough and Lloyd, by using Goldschmidt's method of determining esterification constants, have shown that the introduction of one substituent into the acetic acid molecule has a retarding effect, whatever the nature of the substituent. The introduction of two substituents usually has a more marked effect than one, and three a greater influence than two, when the two or three substituents are alike. A comparison of the esterification constants for the normal fatty acids gave the following values for $E_{MeOH}^{15°}$: formic 1124, acetic 104, propionic 92, and from butyric to stearic values between 50 and 54. The introduction of a carbonyl- group in place of the α-methylene group of a normal fatty acid produces a retardation (Kailan, Monatsh. 1907, 28, 1187 ; Sudborough, Chem. Soc. Trans. 1912, 101, 1227). The introduction of methyl- groups into the molecule of methyl hydrogen succinate also produces a lowering of the esterification constant (Bone, Sudborough, and Sprankling, Chem. Soc. Trans. 1904, 85, 534).

In the case of unsaturated acids, the following generalisations have been drawn (compare Sudborough and Lloyd, Chem. Soc. Trans. 1898, 73, 81 ; Sudborough and Roberts, ibid. 1905, 87,1840 ; Sudborough and Thomas, ibid. 1907, 91, 1033 ; Sudborough and Gittins, ibid. 1909, 95, 315 ; Sudborough and Davies, ibid. 975). 1. An αβ-unsaturated acid is esterified much less readily than its saturated analogue ; in many cases the ratio is 1 : 40. 2. An αβ- unsaturated acid is esterified far less readily than the isomeric acids, in which the double linking is further removed from the carboxyl- group. As a rule, βγ- unsaturated acids are esterified more readily than their saturated analogues ; e.g. βγ-phenylcrotonic acid has $E_{MeOH}^{15°}$ 86.6, and the saturated γ-phenyl-n-butyric acid $E_{MeOH}^{15°}$ 56.25. γδ-Acids and other unsaturated acids, in which the double linking is further removed from the carboxyl- group, are esterified at much the same rate as the corresponding saturated acids ; e.g. E for oleic acid is 54.3, and for palmitic acid 49.7. 3. In most cases the introduction of a substituent into the α- position in the acrylic acid molecule has a greater inhibiting effect than when introduced into the β- position. 4. The effect of a substituent in the cis- position is more marked than in the trans-; thus an acid of the type

$$\begin{array}{c} X\!-\!C\!-\!H \\ \| \\ Y\!-\!C\!-\!CO_2H \end{array}$$

is more readily esterified than the isomeride

$$\begin{array}{c} H\!-\!C\!-\!X \\ \| \\ Y\!-\!C\!-\!CO_2H \end{array}$$
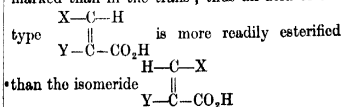
The difference in the rates of esterification of an αβ- unsaturated acid and the saturated analogue, a difference which has been confirmed by Kailan (Monatsh. 1907, 28, 1137) in the case

of cinnamic and hydrocinnamic acids, affords a very convenient method for separating mixtures of the two. This is well shown in the preparation of hydrocinnamic acid. The acid is obtained by the reduction of cinnamic acid, and is liable to contain small amounts of the latter, which are difficult to remove by crystallisation, but a complete separation can be effected by the action of a dilute solution of hydrogen chloride in ethyl alcohol. . The saturated acid is completely transformed into ester, and, under suitable conditions, the unsaturated acid remains unesterified. A similar method can also be used with advantage for the separation of a mixture of an $\alpha\beta$- unsaturated acid and the isomeric $\beta\gamma$-acid ; this method is preferable to the older method used by Fittig, in which the $\beta\gamma$-acid was transformed into the γ-lactone (Sudborough and Thomas, Chem. Soc. Trans. 1911, 99, 2307).

Gyr (Ber. 1908, 41, 4308) has determined the esterification constants of a number of mono-, di-, and tri- substituted acetic acids, and confirms the results obtained by Sudborough and Lloyd. The values, for example, for acetic, phenyl acetic, diphenyl acetic, and triphenyl acetic, at 25° are respectively 7·76, 3·57, 0·20, and 0·001. Gyr worked with absolute methyl alcohol, and recommends boiling some three or four times with small amounts of metallic calcium in order to remove the last traces of water.

Kistiakowsky (Zeitsch. physikal. Chem. 1898, 27, 250) has determined the velocity of reaction of an acid and alcohol in mixtures of the alcohol and water containing hydrogen chloride. In this case the esterification and hydrolysis proceed side by side, and the velocity constants for the two are denoted by K and K'. Then :

$$K = \frac{1}{t} \cdot \frac{\xi}{a} \log_e \frac{\xi}{\xi - x} \text{ and } K' = \frac{1}{t} \cdot \frac{a - \xi}{a} \log_e \frac{\xi}{\xi - x}$$

$$K + K' = \frac{1}{t} \log_e \frac{\xi}{\xi - x}$$

when the amounts of water and alcohol are large compared with the amount of acid present. ξ denotes the gram-molecules of acid transformed into ester at equilibrium, and x the number of gram-molecules transformed at end of time t. K can also be calculated from $K + K'$ by means of equation :

$$K = (K + K') \frac{\xi}{a}$$

The values of K and K' and also the value $\frac{\xi}{a}$ are independent of the original concentration of the organic acid.

The same values for K and K' are obtained when a mixture of acid, alcohol, water, and catalyst, or ester, alcohol, water, and catalyst are used, provided the proportion of water and alcohol and the concentration of the catalyst are kept the same.

The temperature coefficient between $t = 25°$ and $t = 30°$ is about 10 p.c. per degree, using mixtures of alcohol and water containing 13–70 p.c. alcohol.

The values of both K and K' fall on passing from formic to acetic, and again from acetic to monochloracetic.

The effect of the proportion of alcohol and water present is marked. The value of K in the

case of formic acid rises from 0 to 300 as the percentage of alcohol increases from 0 to 91·4, whereas the value for K' falls from 198 to 60, as the percentage of alcohol is increased from 0 to 91·4. In the absence of a catalyst, the velocity of esterification falls as the organic acid is used up, whereas the velocity of hydrolysis is first small, and gradually increases as fresh acid is formed, and both K and K' diminish with an increase in the amount of alcohol present.

Direct method of esterification. The reaction between alcohol and a mineral acid is frequently used as a method for the preparation of ethyl esters of inorganic acids, e.g. ethyl chloride' bromide, nitrite, sulphate (for ethyl bromide, cf. Weston, Chem. Soc. Trans. 1915, 107, 1489 ; Holt, ibid. 1916, 109, 1).

Norris, Watt, and Thomas (J. Amer. Chem. Soc. 1916, 38, 1071) have studied the reaction between different alcohols and dilute solutions of hydrochloric and hydrobromic acids. They find that the rate of formation of esters in the case of primary alcohols tends to decrease as the molecular weight of the alcohol increases. Of the three groups of alcohols, the tertiary are the most, and the primary least, reactive.

Menschutkin, working with the fatty acids (J. pr. Chem. 1881, [ii.] 24, 49 ; ibid. 1882, [ii.] 25, 193 ; Ber. 1897, 30, 2783), was one of the first to draw attention to the relationship between the rate of esterification and the constitution of the acid and of the alcohol, and found that the amount of acid converted into ester in a given time diminished with the complexity of the acid molecule, and also with the complexity of the alcohol molecule. By heating a given amount of acetic acid with equivalent amounts of different alcohols for one hour at 135°, Menschutkin was able to show that, on the whole, a primary alcohol is esterified more rapidly than a secondary, and a secondary than a tertiary. Some of the results obtained by Menschutkin for primary alcohols are not true measures of velocity, as equilibrium had already been obtained within the hour. It is also pointed out that the introduction of side chains or of negative substituents into a primary alcohol also tends to lower the rate of esterification, and the greater the number of such groups introduced the more pronounced is the effect. The introduction of an olefine linking into the molecule of the alcohol in the $\alpha\beta$- position also diminishes the rate of esterification. Subsequent experiments made by heating the alcohol with given weights of acetic anhydride gave similar . results. Still later work with hydroxy-polymethylenes (Chem. Soc. Trans. 1906, 89, 1533), using the acetic anhydride method, indicates that these compounds are esterified more readily than analogous open-chain compounds, e.g. the value for methyl-propyl-carbinol and cyclopentanol are respectively 98 and 189, and that cyclic tertiary alcohols are esterified least readily and primary most readily. The results also indicate that methyl- groups in the o- position with respect to the hydroxyl- group also produce retardation, but not to the same extent as when attached to the carbon atom to which the OH is attached. Michael and Wohlgast (Ber. 1909, 42, 3157) have determined the rates

of esterification of trichloracetic acid with various alcohols at 25° and 50°, and give the following numbers, using the equation for a bimolecular reaction :—

Primary alcohols	$K \times 10^4$ 25°	50°	Secondary	$K \times 10^5$ 25°	Tertiary	$K \times 10^6$ 25°
Methyl . .	3690	24,000	Dimethyl-carbinol .	98	Ter-butyl .	118
Ethyl . .	650	4,210	Methyl-ethyl „	90	Ter-amyl .	248
Propyl . .	725		Methyl-propyl „	76		
Butyl . .	1200		Methyl-hexyl „	109		
*Iso*butyl .	740					
Heptyl . .	1160					
Octyl . .	1860					
Cetyl . .	2500	16,300				

According to Michael, factors which are of importance are : 1. Degree of association of the alcohol ; as this is greater in the case of the simpler alcohols, the rate of esterification would be reduced to a greater extent. 2. Readiness with which the alcohol decomposes into H and R·O· in order to react with the carbonyl- group. 3. The influence of alkyl-groups on the affinity of the R·O· and H for the unsaturated atoms of the carbonyl- group. Michael claims that his results do not afford the slightest evidence for the view that atoms or groups can produce effects by mere filling of space.

As regards the influence of the constitution of the acid on the velocity of esterification, Menschutkin drew the following conclusions as the result of experiments made by heating the respective acids for one hour with *iso*butyl alcohol. The introduction of an alkyl- group into the formic acid molecule invariably produces a retardation in the esterification. The introduction of alkyl- groups into the acetic acid molecule also produces a retardation, and this is greatest when three alkyl- groups replace the three hydrogen, *e.g.* trimethylacetic acid, and is least when only one alkyl- group is introduced. Unsaturated acids of the type of crotonic and cinnamic are esterified less readily than their saturated analogues.

Lichty (Amer. Chem. J. 1895, 17, 27 ; 1896, 18, 590) found, however, that in the case of the chlorinated acetic acids the introduction of a chlorine atom into the acetic acid molecule tends to facilitate the formation of ester when the direct method is used. The presence of an *αβ*- ethylene linking has not the same marked effect in direct esterification as in catalytic esterification (Thomas and Sudborough, Chem. Soc. Trans. 1912, 101, 317). It is obvious that the results obtained by the direct and catalytic methods of esterification are not comparable, and Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 241) have suggested that at least two factors are concerned in the process of esterification when using the same alcohol, viz. (1) strength of the acid esterified ; (2) the presence of substituting groups in close proximity to the carboxyl- group. When the direct method of esterification is used, the former appears to be the determining factor, whereas with the catalytic method the latter is of primary importance ; but in either case both factors are involved. Compare also Flürscheim, Chem. Soc. Trans. 1909, 95, 718.

Rosanoff and Prager (J. Amer. Chem. Soc. 1908, 30, 1895) have also shown that *di*ortho-substituted benzoic acids can be esterified by the direct method, provided they are heated with

excess of the alcohol at a comparatively high temperature (183°) for about 100 hours. The reaction proceeds even at the boiling-point of alcohol, but requires prolonged heating. Rosanoff and Prager determined both the velocity constant K and the reciprocal of the equilibrium constant, viz. $K' = K'/K$. They used different weights of alcohol and acid in each experiment, and by taking the volume of the solution into account, they calculated K by means of the equation :

$$K = \frac{2.3026v}{t\sqrt{(a-b)^2+4ab\mathbf{K}'}} \times$$
$$\log_{10} \frac{2ab - x(a+b-\sqrt{(a-b)^2+4ab\mathbf{K}'})}{2ab \quad x(a+b+\sqrt{(a-b)^2+4ab\mathbf{K}'})}$$

where a and b are the molar concentrations of the acid and alcohol, v is the volume of the mixture in litres, x the number of gram-molecules of the ester formed after time t (in days). The values of K obtained for a few acids are :

Benzoic . . .	.	0.630
2 : 3 : 5-Tribromobenzoic	.	0.370
3 : 4 : 5- „	.	0.900
2 : 4 : 6- „	.	0.088
2 : 4 : 6-Trichlorobenzoic	.	0.031
Acetic . . .	.	1.450
Propionic . .	.	0.950
*Iso*butyric . .	.	1.070
Trimethylacetic .	.	0.180
Chloracetic . .	.	2.460
Dichloracetic . .	.	6.380 ⎱ at 80°
Trichloracetic . .	.	12.000 ⎰

and it is pointed out that in many of these cases an increase in velocity of esterification runs parallel with an increase in the electrolytic dissociation constants of the acids, although the two sets of constants are not proportional.

Michael and Oechslin (Ber. 1909, 42, 317) have determined the amounts of ester formed when various mono- substituted benzoic acids are heated with methyl alcohol in sealed tubes at 135° without a catalyst, but they did not determine the actual constants. They found that many *m*- and *p*- substituted benzoic acids containing negative substituents are esterified somewhat more readily than benzoic acid, but that an *ortho*- substituent, with the exception of Cl, tends to retard esterification, and that the effect is the greatest in the case of the methyl-group.

The following are some of the values obtained after 7 hours : benzoic 11.1, *o*-chlorobenzoic 11.9, *o*-bromobenzoic 10.4, *o*-iodobenzoic 9.7, *o*-nitrobenzoic 10.0, salicylic 7.7, and *o*-toluic 6.2.

The results obtained by Rosanoff and Prager and by Michael and Oechslin are compatible

with the view that at least two factors are concerned in esterification either by the catalytic or the direct method ; that in the former case the chief factor is the presence of substituents in close proximity to the carboxyl- group (steric hindrance) whereas the strength of the acid, as measured by its dissociation constant, is of but secondary importance ; in the direct method the relative values of the two factors are frequently the exact opposite. (Note : The dissociation constant for s-trichlorobenzoic acid is not known.) The results do not justify the conclusion drawn by both Rosanoff and Michael, that substituents do not retard esterification by mere space filling.

For direct esterification of dibasic acids, *see* Kailan (Zeitsch. physikal. Chem. 1915, 89, 676).

The reaction between a mercaptan and an acid is analogous to that between an alcohol and an acid, and the product is the ester of a thio-acid. The reaction has been studied in detail by L. S. Pratt and E. E. Reed (J. Amer. Chem. Soc. 1915, 37, 1934) at a temperature of 243°, and using different mercaptans. The limiting values are much less than when the corresponding alcohols are used, and tend to diminish as the molecular weight of the alcohols increases.

Other methods for preparing esters. Esters which cannot be obtained by direct esterification, *e.g.* the esters of diortho- substituted benzoic acids, can be prepared by the following methods : 1. Action of the alcohol on the acid chloride or acid anhydride. The latter action is accelerated by the presence of small amounts of a strong acid (Reychler, Bull. Soc. chim. Belg. 1907, 21, 428).. 2. Action of the alkyl iodide on the dry silver salt, or, in the case of aromatic acids, by the action of alkyl chlorides on dry potassium salts in the presence of a trace of a base such as triethylamine. Benzyl benzoate is readily prepared by heating together at 95°–100° potassium benzoate (100), benzyl chloride (120), and triethylamine (1). 3. Action of methyl sulphate on an aqueous solution of the sodium salt of the acid (Werner and Seybold, Ber. 1904, 37, 3658). 4. Action of an ethereal solution of diazomethane on the acid.

Sulphonic acids. Sulphonic acids do not give good yields of esters when warmed with alcohol alone or with alcohol and a mineral acid. This is probably due to the fact that the ester formed immediately reacts with the alcohol, giving the free acid and an ether :

$$C_6H_5 \cdot SO_2 \cdot OMe + MeOH = C_6H_5 \cdot SO_2 \cdot OH + Me_2O$$
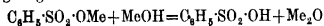
(comp. Krafft and Roos, Ber. 1893, 26, 2823 ; Wegscheider and Furcht, Monatsh. 1902, 23, 1094). The esters are not formed when the sodium salt of the acid is warmed with alkyl iodide and alcohol (Wegscheider and Furcht) ; but can be obtained by the action of methyl sulphate on the acid or by the action of the alcohol on the acid chloride at low temperatures (Krafft, Ber. 1892, 25, 2256).

Esters of dibasic acids. A dibasic acid can give rise to both an acid and a normal ester, *e.g.* $CO_2H \cdot CH_2 \cdot CO_2H \rightarrow CO_2H \cdot CH_2 \cdot CO_2Me$ and $CO_2Me \cdot CH_2 \cdot CO_2Me$. With the exception of diortho- substituted aromatic dibasic acids, the normal esters can be obtained by the Fischer-Speier method of esterification. For the preparation of the acid esters, the following methods

are resorted to : 1. Addition of alcohol or of sodium alkyl oxide to the acid anhydride. 2. Partial hydrolysis of the normal ester. 3. Partial esterification of the acid. 4. The action of alkyl iodides on the acid silver salts, if these can be prepared, or on the acid potassium salts. In the case of a symmetrical dibasic acid, the same acid ester is formed by all these methods, although, in most cases, except those coming under the first heading, the yields are not very good, as free acid and normal esters are also formed, and the separation is not always easy.

With an unsymmetrical dibasic acid, two isomeric acid esters (the a and the b) [1] can exist, and which of these is formed depends largely on which method of preparation is used. Wegscheider has carried out numerous experiments (comp. Monatsh. 1895, 16, 75 ; 1897, 18, 418, 629 ; 1899, 20, 685 ; 1900, 21, 621, 638, 787 ; 1902, 23, 317, 357, 369, 393, 405 ; 1903, 24, 413, 915 ; 1905, 26, 1039 ; 1906, 27, 487, 777 ; 1907, 28, 819 ; 1908, 29, 525, 531, 535, 541, 557 ; sulphonated benzoic acids, *ibid.* 1902, 23, 1093 ; tribasic acids, *ibid.* 1910, 31, 1253) on the following acids : hemipinic (3 : 4-dimethoxyphthalic), nitrohemipinic, camphoric, nitro-, bromo-, amino-, and hydroxy-terephthalic, 3- and 4-nitrophthalic, 4-hydroxyphthalic, phthalonic, homophthalic, aspartic, phenyl-succinic, and papaverinic, and has drawn the following conclusions under the assumption that the two carboxylic groups differ appreciably as regards their relative strength : 1. By the addition of alcohol to the anhydride and by the action of alkyl iodides on the acid potassium or acid silver salts, the stronger carboxyl- group is esterified, so that under these conditions a-acid esters are formed. If there is but little difference in the relative strengths of the two carboxyl-groups, then a mixture of the two acid esters is obtained, but the a- compound preponderates ; *e.g.* $C_6H_2(CO_2H)_2(OMe)_2(1:2:3:4)$ gives, by these methods, the acid ester :

$$C_6H_2(CO_2H)(CO_2Et)(OMe)_2$$
$$123.4$$

$$CO_3H \cdot C_6H_3 \begin{cases} CO & (2) \\ CO & (3) \end{cases} O \text{ gives } C_6H_3 \begin{cases} CO_3H & (1) \\ CO_3Me & (2) \\ CO_3H & (3) \end{cases}$$
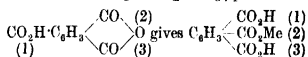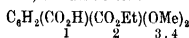
Exception : phenyl succinic anhydride. Diazo-methane and the acid give mainly neutral ester, but also small amounts of acid ester derived from the stronger carboxyl- group. 2. By the process of catalytic esterification the carboxylic acid group, which is freer from adjacent sub-stituents, is esterified first ; thus opianic acid gives the b- ester $C_6H_2(CO_2Et)(CO_2H)(OMe)_2$, $123:4$ but neutral ester and small amounts of the a-isomeride may also be formed, especially if the conditions are such that anhydride formation can occur. The same rule holds good for direct esterification if the possibility of anhydride formation is excluded. 3. The addition of sodium alkylate in the absence of alcohol and water to the anhydride yields the b- acid ester, with appreciable amounts of the isomeride. 4. The partial hydrolysis of the neutral ester gives the acid ester, which is difficult to prepare

[1] The term b- ester is given to the acid ester with the higher dissociation constant, and the isomeride is termed the a- (Ber. 1902, 35, 4829 ; 1903, 36, 304).

by the method of catalytic esterification; *e.g* dimethylhemipinate gives the *a*-acid ester. Exceptions : the hydrolysis of methyl hydroxy-terephthalate, 4-hydroxyphthalate, 4-nitroph-thalate, aminoterephthalate, phthalonate.

For formation of esters of phthalic acid in presence of hydrochloric acid and hydrolysis of the esters, *see* Wegscheider and Amann (Monatsh. 1915, 36, 549 and 633).

In the case of the majority of symmetrical dibasic acids the two carboxylic groups are esterified at the same rate; in other words, the replacement of OH by OEt does not affect the rate of esterification. In the case of both maleic and oxalic acids, however, there is a retardation produced by the conversion of one of the CO_2H groups into a CO_2Et. This is attributed by Kailan (Zeitsch. physikal. Chem. 1914, 87, 619) to the proximity of the two carboxylic groups to one another, and as the retardation is greater in the case of maleic acid, it is argued that in this acid the two carboxylic groups are closer than in oxalic acid.

Theories of esterification.—*Direct method :* The reaction between the acid and alcohol is not a simple ionic reaction, since the acid with the highest dissociation constant is not neces-sarily esterified most readily, and in the case of a dibasic acid it is not always the stronger CO_2H group which is esterified first. The view usually accepted at the present time is that an additive compound of alcohol and acid of the type

$$R \cdot C \!\!\!\begin{array}{c} \diagup OEt \\ \diagdown OH \end{array}$$
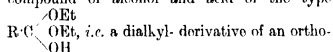
i.c. a dialkyl- derivative of an ortho-carboxylic acid, is first formed by the addition of a molecule of alcohol to the carbonyl- group of the acid (Wegscheider, Monatsh. 1895, 16, 137 ; Henry, Ber 1877, 10, 2041). Michael suggests that before this additive compound is formed an unstable ' Kekulé double molecule ' is formed, perhaps by the coming into play of the two latent valencies of the oxygen atoms :

$$R \!\!\!\begin{array}{c} \diagup C = 0 \diagup OH \\ \diagdown OH \quad\ \diagdown Et \end{array}$$
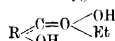
It is well known that many esters can form additive compounds with sodium ethoxide, and, therefore, presumably with ethyl alcohol, although compounds of the latter type have not been isolated. Pechmann (Ber. 1898, 31, 503) has been able to show that the esters of diortho-substituted benzoic acids cannot yield additive compounds with sodium ethoxide, probably owing to the space filling (steric hindrance) of the group in the ortho- position ; by analogy, the diortho- substituted acids would not yield the orthocarboxylic acid derivative at all readily, and this would account for the fact that diortho-substituted benzoic acids are not readily esterified.

Catalytic esterification. According to Michael, the processes of direct and catalytic esterifica-tion are essentially different ; the former is a reaction between the organic acid and alcohol, and the latter a reaction between the organic acid and an additive compound of the alcohol and catalyst (Ber. 1909, 42, 312). This reaction does not consist of addition to the carbonyl-group of the acid, but in union of the acid with the alcohol-catalyst complex to form a large ' double molecule,' which decomposes immedi-ately into ester, water, and catalyst. The fact

that esterification is facilitated by the presence of the catalyst is accounted for by the assump-tion that the alcohol-catalyst complex contains a greater store of energy, is therefore more re-active than the alcohol itself, and can more quickly develop the maximum entropy of the alcohol-acid system. It is questionable whether these views are in harmony with the facts estab-lished by Wegscheider, viz. that the same acid ester is obtained from an unsymmetrical dibasic acid, whether the direct or catalytic method of esterification is adopted, provided that anhy-dride formation is excluded. Goldschmidt also comes to the conclusion that the two processes are essentially different (Zeitsch. Elektrochem. 1909, 15, 4). He claims to have shown that the presence of sodium trichloracetate does not depress the velocity of esterification of trichlor-acetic acid by the direct method, and, therefore, the direct esterification cannot be a simple case of hydrion catalysis. Later experiments of Sudborough and Turner show that the presence of salts of trichloracetic acid does diminish the rate of esterification of the acid, and hence Goldschmidt's conclusion is not justified. The fact that in direct esterification the strength of the acid is an important factor is compatible with the view that the organic acid itself plays the same part in direct esterification that the catalyst does in catalytic esterification. This view agrees again with the fact that the reaction in certain cases of direct esterification is bimolecular (Goldschmidt, Ber. 1896, 29, 2208), provided the reaction is not between the ions of acid and alcohol.

Kailan (Monatsh. 1908, 29, 799) is also of opinion that the processes of direct and catalytic esterification are not analogous, since the addition of a small amount of water increases the rate of esterification of trichloracetic acid by the direct method, but diminishes the activity of trichloracetic acid when it is used as a catalyst.

Various views are held with regard to the function of the catalyst. Goldschmidt and Uddy (Zeitsch. physikal. Chem. 1907, 60, 728 ; comp. also Ber. 1906, 39, 711, and Zeitsch. physikal. Chem. 1910, 70, 627) conclude that the hydrions of the catalyst are the active agents, since the activity of different acids is in the order of their relative strengths, *e.g.* the relative values of the acids hydrochloric, picric, trichloracetic, and dichloracetic as catalysts are indicated in the order given, and the addition of salts of the acid used as catalyst diminishes the activity of the catalyst. They further conclude that the hydrions unite with the alcohol, and that the complex ion $(C_2H_6O,\overset{+}{H})$ is the active agent. They suggest the following modified formula for calculating the velocity constant :—

$$K \cdot c = \frac{1}{t}(n+r+a) \, \log_e \frac{a}{a-x} - x$$

where c = concentration of catalyst, n = concentration of water, and r = hydrolytic constant of the complex alcohol ion for

$$(C_2H_6O,\overset{+}{H}) \quad r = 1 \cdot 5.$$
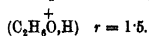
The constants obtained by means of this equation agree better, and do not show the tendency to decrease as t increases, a tendency which is marked when the constants calculated

by means of the ordinary equation for a unimolecular reaction are used.

A marked exception to the depressing effects of the addition of salts is met with in the case of hydrogen chloride, where the addition of chlorides such as calcium chloride, tetramethyl-ammonium chloride, and aniline hydrochloride, have no appreciable effect on the catalytic activity of hydrogen chloride (Goldschmidt ; Sudborough).

Many chemists are of opinion that in catalytic esterification, as in catalytic hydrolysis of esters by means of mineral acids (see art. on HYDRO-LYSIS), a complex is formed between the substance transformed (acid in esterification and ester in hydrolysis) and the catalyst. This compound is probably an oxonium salt containing quadra-

valent oxygen, e.g. $R \cdot C \underset{OH}{\overset{O \underset{Cl}{\overset{H}{\diagup}}}{\diagdown}}$. The salt,

only small amounts of which may be present, is ionised into $(R \cdot CO_2H_2H)$ and $\overset{+}{Cl}$, and the esterification proceeds by the reaction of the complex cation with the alcohol (Acree and Johnson, Amer. Chem. J. 1907, 38, 334) ; e.g. :

$$(R \cdot CO_2H_2H) + C_2H_5OH = R \cdot CO_2Et + H_2O + \overset{+}{H}$$
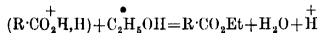
and not with the ions of the alcohol as suggested by Lapworth. This reaction is more rapid than the simple reaction between the acid and alcohol, and in this way the accelerating effect of the catalyst is accounted for.

The retarding effects produced by small amounts of water are, according to Lapworth (Chem. Soc. Trans. 1908, 93, 2167, 2196), due to the water competing with the organic acid for the catalyst, and giving rise to the complex ion (H_2O,H), which is not catalytically active. The fact that in alcohol containing water, the velocity of esterification at constant volume decreases more rapidly than the concentration of the catalyst (Goldschmidt and Uddy, Zeitsch. physikal. Chem. 1907, 60, 735 ; Kailan, Monatsh. 1906, 27, 543, 997 ; Annalen, 1907, 351, 186), is also held to be opposed to the view that a complex hydrion is formed with the alcohol.

Work on the catalytic activity of strong acids tends to show that this activity is exerted in two ways : (a) by means of hydrions ; (b) by the non-ionised acid, and that the effect due to the non-ionised acid is greater for highly ionised than for slightly ionised catalysts. In methyl and ethyl alcohol the retarding influences of water on esterification is of much the same magnitude for different acids, and this is held to support the view that an intermediate compound of alcohol and catalyst plays a most important part in the change (Goldschmidt and Thuesen, Zeitsch. physikal. Chem. 1912, 81, 30).

Compare also Snethlage, ibid. 1913, 85, 211 ; 1915, 90, 91 and 139 ; Acree, Amer. Chem. J. 1912, 48, 352 ; Dawson and others, Chem. Soc. Trans. 1913, 103, 2135 ; 1914, 105, 1093 ; 1915, 107, 1426 ; 1916, 109, 1262 ; McBain and Coleman, ibid. 1914, 105, 1517 ; H. S. Taylor, Zeitsch. Electro. Chem. 1914, 20, 201.

(For the conversion of acid amides into esters, and for the transformation of methyl into ethyl VOL. II.—T.

esters, both processes of alcoholysis, see art. HYDROLYSIS.) J. J. S.

ESTON. Trade name for basic aluminium acetate. Used as an antiseptic powder in dressing wounds.

ESTORAL v. SYNTHETIC DRUGS.

ESTRAMADURITE v. FERTILISERS.

ETA (E) ACID. 1-Naphthylamine-3 : 8-disulphonic acid v. NAPHTHALENE.

ETELEEN. Trigallic acetal.

ETHAL v. WAXES.

ETHYL C_2H_5 or $CH_3—CH_2$ is a univalent basylous radical not known in the free state, the body C_4H_{10} or $(C_2H_5)_2$ which was named, ethyl (afterwards diethyl) by its discoverer, Frankland (Chem. Soc. Trans. 2, 263), being now regarded as butane.

Ethyl acetamide v. Ethylamine (infra).

Ethyl acetate v. ACETIC ACID.

Ethyl acetoacetate v. KETONES.

Ethyl alcohol v. ALCOHOL.

Ethyl antimonite $(C_2H_5O)_3Sb$; b.p. 115°-120° ; from action of C_2H_5OH upon Sb_2O_3 in presence of anhydrous $CuSO_4$; colourless liquid (McKey, Chem. Soc. Trans. 1909, 95, 604).

Ethyl arsenite $(C_2H_5O)_3As$. A liquid formed by action of C_2H_5OH upon As_4O_6 in presence of anhydrous $CuSO_4$, the yield being 4·5 p.c. (Lang, McKey, and Gortner, Chem. Soc. Trans. 1908, 93, 1368). According to Crafts (Bull. Soc. chim. 1870, ii. 14, 99), it is obtained in very small yields by

(1) Action of Et_3SiO_3 upon As_4O_6 at 200° ;
(2) Action of Ag_3AsO_3 upon EtI at 150° ;
(3) Action of $AsBr_3$ upon NaOEt.

Auger (Compt. rend. 1906, 143, 907) obtained a yield of 1·2 p.c. by heating EtOH and As_4O_6 in a sealed tube far above the boiling-point of the alcohol.

Ethyl arsenate. A liquid boiling above 200° with partial decomposition. Decomposed by water immediately. Formed by heating together in sealed tubes at 100° Ag_3AsO_4 and EtI (Crafts, Bull. Soc. chim. 1870, ii. 14, 99).

Ethyl boride $(C_2H_5)_3B$. Triethyl boride, Borethyl ; b.p. 95° ; sp.gr. 0·696 at 23° ; V.D. at 132° = 3·581 ; at 101·6° = 3·76 ; calc. = 3·399. From action of $Zn(C_2H_5)_2$ upon $(C_2H_5)_3BO_3$, or from BCl_3 and $Zn(C_2H_5)_2$ (Frankland, Trans. Roy. Soc. 1862, 167 ; Proc. Roy. Soc. 1876, 25, 165).

A spontaneously inflammable, colourless liquid burning with green flame ; decomposed by HCl, evolving C_2H_6, and forming $B(C_2H_5)_2Cl$. Is slowly decomposed by water, and destroyed by HNO_3, with formation of boric acid. Absorbs NH_3, forming an oily liquid $NH_3B(C_2H_5)_3$ of an aromatic odour, which is fairly stable even in contact with O. $B(C_2H_5)_3$ absorbs O and forms $B(C_2H_5)_3O_2$; b.p. 125°. This, by the action of water, yields ethylboric acid $B(C_2H_5)(OH)_2$, a crystalline solid resembling naphthalene in appearance ; can be sublimed at 40° ; has a sweet taste, and acid action, but does not combine with bases. By action of $Zn(C_2H_5)_2$ upon this body we get $B(C_2H_5)(OC_2H_5)_2$ and $B(OC_2H_5)_3$; b.p. 112° ; V.D. (dissoc.) 2·78. By further action of $Zn(C_2H_5)_2$ upon ethylboric acid we get $B(C_2H_5)_2OC_2H_5$; b.p. 102° ; V.D. = 3·914. Water converts this into $B(C_2H_5)_2OH$, a spontaneously inflammable liquid, which absorbs oxygen, yielding $B(C_2H_4O)C_2H_5 \cdot OH$; m.p. 8°.

Ethyl bromide C_2H_5Br. *Hydrobromic* or *Bromhydric ether*; m.p. $-116\cdot0°$ (Ladenburg and Krugel, Ber. 32, 1818), $-125\cdot5°$ (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. $38\cdot22°$ (corr.) (Thorpe and Rodger, Phil. Trans. 1894, A, 11, 472); sp.gr. $1\cdot4189$ at $15°$ (Mendéleeff), $1\cdot4733$ at $0°$ (Pierre), $1\cdot4685$ at $13\cdot5°$; crit. temp. $236°$ (Pawlewski, Ber. 16, 2633).

Preparation.—1. By action of P and Br upon alcohol (Serullas, Ann. Chim. Phys. [2] 34, 99). 40 parts red P and 160 parts absolute alcohol are slowly mixed with 100 parts Br, kept cool until all action is over; the mixture is then distilled, and the distillate purified by washing with water and rectification (Personne, Compt. rend. 52, 468).—2. Absolute alcohol is heated with Br and distilled, and the distillate is freed from excess of Br by washing with KOH and redistillation (Lowig, Annalen, 3, 288).—3. 4 parts KBr and 5 parts of a mixture of 2 parts H_2SO_4 and 1 part alcohol of 96 p.c. are distilled, and distillate purified as above (De Vrij, J. 1857, 441, Tabourg, Bull. Soc. chim. 1911, [iv.] 9, 124). Weston (Chem. Soc. Trans. 1915, 108, 1489) has given details of a modification of De Vrij's method, using sodium bromide in place of potassium bromide and paying attention to the rate of heating, whereby yields of 80–90 p.c of the theoretical amount of pure ethyl bromide can be obtained (*cf.* Holt, Chem. Soc Trans. 1916, 109, I.).—4. C_2H_4 in presence of $AlBr_3$ at $0°$ combines with HBr to form C_2H_5Br (Gustavson, J. Russ. Phys. Chem Soc 16, 95). To prepare pure C_2H_5Br, the commercially pure bromide is shaken with H_2SO_4 and allowed to separate. It is then shaken with dilute alkali and distilled with 10 p.c of sweet almond oil (Adrian, Chem. Zentr. 1895, i. 20).

Ethyl bromide is a colourless liquid with a sweet taste, and burning after-taste. Its vapour has anæsthetic properties (Robin, Compt. rend. 34, 649; Webster, Bio. Chem. J. 1906, i 328; Cole, J. Physiol. 29). It is slightly soluble in water, and miscible with alcohol and ether. The vapour is decomposed by heat, yielding C_2H_4 and HBr, or, if the temperature be higher, C is deposited (Löwig). Burns in air with a green flame, evolving HBr. By introduction of Cl two isomeric bodies of the composition C_2H_4ClBr, b.p. $84\cdot5°$ and $104°$-$108°$, and 2 isomerides of composition $C_2H_3Cl_2Br$, b.p. $137°$, $151°$ (Lescœur, Bull. Soc. chim. 1878, 29, 483) are obtained. At $100°$ Br reacts, forming $CH_2Br\cdot CH_2Br$, whilst at $200°$ $CH_3\cdot CHBr_2$ is the product (Meyer and Müller, Ber. 24, 4247; J. pr. Chem. [2] 46, 161). By action of Br and P upon alcohol. we get, further, $C_2H_4Br_2$, b.p. $160°$; $C_2H_3Br_3$, b.p. $180°$; $C_2H_2Br_4$, b.p. $196°$-$200°$ (Bertrand, Finot, Bull. Soc. chim. 34, 28) (*v. Ethylene bromide*). Heated with $AlBr_3$, yields successively $C_2H_4Br_2, C_2H_2Br_4$, and C_2Br_6 (Mouneyrat, Compt. rend. 127, 109). With ammonia it yields $NH_4(C_2H_5)$,HBr; and with ethylamine, diethylammonium bromide $NH(C_2H_5)_2$,HBr; similarly, with diethylamine, it yields $N(C_2H_5)_3$HBr.

Ethyl chloride C_2H_5Cl. *Chlorhydric* or *Hydrochloric ether*; m.p. $-142\cdot5°$ (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. $12\cdot5°$ (Regnault, J. 1863, 67); crit. temp. $187\cdot2$; crit. press. $51\cdot7$ atm. (Berthoud); sp.gr. $0\cdot9214$ at $0°$; $0\cdot9176$ at $8°$, $0\cdot920$ at $0°$ (Pierre), $0\cdot851$

at b.p. (Ramsay, Chem. Soc. Trans. 35, 470); S.V. $75\cdot8$ (Kopp). (Robiquet and Colin, Ann. Chim. Phys. [2] 1, 343; Regnault, *ibid.* 71, 355; Kühlman, Annalen, 33, 108; Löwig, Pogg. Ann. 14, 346; Gm. 7, 367; Gerh. 11, 308.) For a table of its vapour pressure between $-30°$ and $+100°$, see Henning, J. Soc. Chem. Ind. 1920, I. T

Known as far back as 1500, and its preparation described by Glauber in 1648. From alcohol by the action of S_2Cl_2 or metallic chlorides (Rouelle [1759]); from alcohol and HCl (Basse [1801]). Composition first ascertained by Robiquet and Colin. Also formed by action of Cl upon C_2H_6 (Darling, Annalen, 150, 216), and of HCl upon ether in sealed tubes (Berthelot).

The action of HCl upon alcohol gives a very poor yield of C_2H_5Cl, unless $ZnCl_2$ is added to the alcohol before passing in HCl (Groves, Chem. Soc. Trans. 1874, 636). Krüger (J. pr. Chem. [2] 14, 193) recommends that a mixture of 1 part of $ZnCl_2$ in 82 parts of alcohol should be saturated with HCl gas in the cold, and then heated to boiling, HCl being passed in during distillation. A reflux condenser stops the alcohol vapour, and the C_2H_5Cl passes on and is collected in a well-cooled receiver.

The formation of C_2H_5Cl in this process is partly due to the action of HCl upon alcohol, and partly to the union of the nascent C_2H_4 with HCl (Schorlemmer, Chem. Soc. Trans. 1875, 308); this view is sustained by the fact that if amyl alcohol be thus treated, both primary and secondary amyl alcohol are produced, and the latter can only be formed from the radical C_5H_{10}. Ethyl chloride is also formed by the action of PCl_5 upon alcohol, and also, to some extent, by the action of Cl upon alcohol. Hence the formation of ethyl chloride in the manufacture of chloral.

It is a colourless mobile liquid; has a pungent ethereal smell, and a sweetish taste, is inflammable and burns with a green-edged flame, evolving HCl. It is sparingly soluble in water (1 part in 3000), but mixes readily with alcohol and ether. It dissolves phosphorus, sulphur, fats, oils, and many resins. It combines with many metallic chlorides—*e.g.* $SbCl_5$, Fe_2Cl_6 —to form crystalline compounds. Mainly used for Ethylation in the manufacture of dye stuffs and drugs, and as a refrigerant and solvent.

It is used in medicine like ether, but, on account of its volatility, it is mixed with an equal volume of alcohol, and is then known as 'alcoholised muriatic ether, B.P.' It is decomposed at a red heat into C_2H_4 and HCl; at higher temperatures carbon separates, and CH_4,H, and HCl are set free. Strong HNO_3, when boiling, liberates HCl and forms $C_2H_5NO_2$ in small quantity (Thénard, Boullay). SO_3 absorbs it, forming $SO_3\cdot C_2H_5Cl$, a fuming liquid, b.p. $130°$ —probably the three isomerides $C_2H_4O\cdot SO_3\cdot Cl$, $CH_3\cdot ClCH_2\cdot SO_2\cdot OH$, and $CH_2(OH)\cdot CH_2SO_2\cdot Cl$ (Purgold, Zeitsch. Chem. 1868, 669; Ber. 6, 502). When vapour of C_2H_5Cl is passed through boiling H_2SO_4, HCl is evolved (Thénard), also C_2H_4 and SO_2 (Boullay). When the vapour is led through a tube containing heated soda-lime, a mixture of CH_4 and H is evolved, and $NaC_2H_3O_2$ and Na_2CO_3 are formed (L. Meyer, Annalen, 139, 282), while, according to Dumas and Stas, C_2H_4 and NaCl are formed. On

AgNO$_3$,C$_2$H$_5$Cl has no action until after prolonged contact, but even after some months only a very small quantity of AgCl is formed (Thénard, Boullay) ; but AgCl is rapidly thrown down when C$_2$H$_5$Cl is heated with a solution of AgNO$_3$ in sealed tubes (G. C. Foster).

Heated with bromine and iron wire at 100°, C$_2$H$_5$Br and ethylene dibromide are formed (V. Meyer and Petrenko-Kritschenko, Ber. 25, 3307).

NH$_3$ has only a slight action at ordinary temperatures, but on heating a mixture of NH$_3$ and C$_2$H$_5$Cl, ethylene and a deposit of NH$_4$Cl are formed (Dumas and Stas, Ann. Chim. Phys. 73, 154). When a mixture of ethereal NH$_3$ and C$_2$H$_5$Cl is exposed to sunlight, crystals of ethyl-amine hydrochloride separate (Stas). When heated with alcoholic NH$_3$ to 100° in sealed tubes, NH$_2$(C$_2$H$_5$),HCl is also produced, together with traces of NH(C$_2$H$_5$)$_2$,HCl and N(C$_2$H$_5$)$_3$,C$_2$H$_5$Cl (Groves, Chem. Soc. Trans. 1861, 13, 331). KOH slowly removes Cl from C$_2$H$_5$Cl, yielding (in aqueous sol.) alcohol and KCl. Alcoholic KOH and C$_2$H$_5$Cl heated to 100° in sealed tube deposits KCl and forms (C$_2$H$_5$)$_2$O (Balard, Ann. Chim. Phys. [3] 12, 302). Passed into heated sol. of K$_2$S, ethyl sulphide is formed ; with alcoholic KHS, mercaptan is formed (Regnault).

Chlorine in the sunlight yields di-, tri-, tetra-, penta-, and hexa- chloro- derivatives of ethane (Regnault) ; of the dichloro- derivatives CH$_3$·CHCl$_2$ is the main product. If, however, ethyl chloride is heated with a halogen carrier, CH$_2$Cl·CH$_2$Cl is the chief product (D'Ahns and Kautzsch, J. pr. Chem. [2] 1909, 80, 305 ; Staedel ibid. 303 ; Ber. 6, 1403 ; Meyer and Muller, J. pr, Chem. [2] 46, 161).

Trichlorethane C$_2$H$_3$Cl$_3$.

1. *Chlorethylene chloride* CH$_2$Cl·CHCl$_2$; b.p. 115° (Pierre, Annalen, 80, 127), 113·7° at 760 mm. (Stadel, Ber. 15, 2563), 113·5°–114° at 753·2 (Schiff, Annalen, 220·97) ; sp.gr. 1·4223 at 0° (P.), 1·4577 at 9·4°/4°, 1·2945 at 113·5°/4° (Schiff, 1·4406 at 25·6° ; μ$_A$=1·4719 at 22° Rα=42·26 (Kanonnikow), from C$_2$H$_3$Cl (Regnault, Ann. Chim. Phys. [2] 69, 151), or CHCl$_2$·CH$_3$ (Meyer and Muller, J. pr Chem. [2] 46, 174), and SbCl$_5$.

2. *Ethenyl trichloride* CH$_3$·CCl$_3$; b p. 74·5° (Geuther, J. 1870, 435) ; 74·1° at 760 mm. (Städel, Ber. 15, 2563) ; sp.gr. 1·3465 at 0° (Pierre, Annalen, 80, 127), 1·372 at 16° (Regnault, Annalen, 33, 317), 1·3657 at 0°, 1·3249 at 26° ; μ$_A$=1·4199 at 21° ; Rα =42·0 (Kanonnikow) ; by the chlorination of ethyl chloride (Regnault, ibid. 33, 317). Decomposed by sodium ethoxide, giving C$_2$H$_3$Cl·O·C$_2$H$_5$, C$_2$H$_3$(O)$_2$, and CH$_3$(OEt)$_3$.

Tetrachlorethane C$_2$H$_2$Cl$_4$.

1. *as-*CH$_3$Cl·CCl$_3$; b.p. 135° (Regnault, Ann. Chim. Phys. [2] 69, 162), 138·6° (Pierre, Annalen, 80, 130), 135·1° (corr.) (Geuther, Brockhoff, J. 1873, 317) ; sp.gr. 1·6116 at 0° (P.), 1·576 at 19° (R.), 1·5825 at 0°, 1·5424 at 26° ; . μ$_A$ at i°=1·4772−0·0004371 ; Rα =50·72 (Kanonnikow). Formed by chlorination of ethyl chloride (Laurent, Annalen, 22, 292) ; or action of Cl upon CH$_2$Cl CHCl$_2$ (Regnault) ; by heating at 110° acetylene tetrachloride and AlCl$_3$ (Mouneyrat, Bull. Soc. chim. 1898, 19, 499).

Decomposed by sodium ethoxide into C$_2$HCl$_3$·O·C$_2$H$_5$ and CH$_2$(OC$_2$H$_5$)CO$_2$Na.

2. *s-*CHCl$_2$·CHCl$_2$; b.p. 147·2° ; sp.gr. 4°/4°=1·6208, 17°/17°=1·6013 ; μ$_D$ at 17°=1·495587±0·000006 (Veley, Proc. Roy. Soc. 1910, B 82, 217) ; Rα =50·6 (Kanonnikow). From C$_2$H$_2$ and SbCl$_5$ (Berthelot, Jungfleisch, Annalen, Suppl. 7, 264), from dichloraldehyde and PCl$_5$ (Paternò, Pisati) ; from ethylene chloride and AlCl$_3$ at 75° if Cl and C$_2$H$_2$ be led into the mixture (Mouneyrat) ; by long heating yields HCl and C$_6$Cl$_6$.

If S$_2$Cl$_2$ and 1 p.c. of its weight of reduced iron be saturated with Cl, and if the excess Cl be removed with CO$_2$, and then dry acetylene be passed in at a temperature of 40°, and the cycle repeated until no more C$_2$H$_2$ is absorbed, *sym*-tetrachloroethane, pentachloroethane, and hexachloroethane are produced, the two latter in small quantity (Michel, Zeitsch. angew. Chem. 1906, 19, 1095). The *sym*-tetrachlorethane is distilled off from the mixture, either alone or in steam (D. R. P. 174068 ; Chem. Soc. Abstr. 1906, i. 169).

Pentachlorethane CHCl$_2$ CCl$_3$; b.p. 159·1° (corr.) ; 161·7° at 760 mm. (Stadel) ; m.p. −18° ; sp.gr. 1·7089 at 0°, 1·6926 at 10·15°/4° (Thorpe, Chem. Trans. 37, 192) ; μ$_A$ = 1·4871 at 25·1° ; Rα = 59·05 (Kanonnikow). By action of chlorine upon C$_2$H$_5$Cl also from chloral and PCl$_3$ (Paternò, Annalen, 151, 117), or AlCl$_3$ (Mouneyrat, Bull Soc. chim. 1898, 19, 260).

Hexachlorethane CCl$_3$·CCl$_3$ (*v. Carbon trichloride*, art. CARBON).

(For mixed halogen derivatives of ethane, see Mouneyrat, Bull. Soc. chim. 1898, 19, 499 ; Swartz, Rec. trav. chim. 17, 234 and 235 ; Bull. Acad. Roy Belg. 36, 519 ; ibid. 1909, 60 and 728 ; ibid. 1899, n. 281 ; Elbs and Newmann, J. pr. Chem. 1898, 58, 245 ; Biltz, Ber. 1902, 35, 3524 ; Lemoult, Compt rend. 1903, 136, 1333 ; Besson, Bull. Soc. chim. [3] 11, 920 ; Nef, Annalen, 298, 353, 354, 358, and 360 ; Thele and Peter, ibid. 369, 149 ; Lawrie, Amer. Chem. J. 1906, 36, 487.)

Ethyl *iso*cyanate. *Ethyl carbimide,* C$_2$H$_5$N : C : O ; b.p. 60° ; sp.gr. 0·8981 ; heat of formation (Lemoult, Compt. rend. 1898, 126, 43) ; absorption spectrum (Hartley, Dobbie and Walker, Chem. Soc. Trans. 1901, 856). By the action of dry KCNO upon KC$_2$H$_5$SO$_4$ at 180°–250° (Wurtz, Ann. Chim. Phys. 1854 [3] 42, 43) ; distillate is a mixture of *iso*cyanate and *iso*cyanurate, which can easily be separated by distillation. By passing CNBr into absolute alcohol and ether (Ponomarew, Ber. 1882, 15, 515 ; Mulder, Rec. trav. chim. 1, 210 ; 2, 133) ; by passing CNBr (Mulder, ibid. 3, 306) or CNCl (Cloez, Compt. rend. 44, 428 ; Annalen, 102, 355) into C$_2$H$_5$ONa in absolute alcohol ; by the action of diazomethane on *sym*-ethylnitrourea (Degner and Pechmann, Ber. 1897, 30, 653) ; by heating the mercuric chloride derivative of ethyl thiolcarbamate (Anschütz, Annalen, 1908, 359, 202).

In 1895 Nef (ibid. 287, 310) showed that the compound hitherto known as ethyl cyanate was ethyl *iso*cyanate. Ethyl *iso*cyanate is a mobile liquid having a suffocating smell. It is decomposed by water into diethylcarbamide, and by ammonia into ethylcarbamide.

Ethyl cyanide. **Propionitrile** C$_2$H$_5$·C : N,

m.p. ⌐103·5° (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. 98·1° (corr.) (Engler, Annalen, 133, 153); 97·08°‚ (corr.) (Thorpe, Chem. Soc. Trans. 37, 205); sp.gr. 0·8010 at 0°, 0·7938 at 7·36°/4° (Thorpe), 0·7015 at 97°/4° (Schiff, Ber. 19, 567); H. C. 446·7 Cals. (Berthelot and Petit, Compt. rend. 108, 1217); latent heat of vapourisation (Louguinine, Chem. Zentr. 1900, i. 451); molecular refraction 25·10 (Brühl, Zeitsch. physikal. Chem. 16, 214; Eykman, Rec. trav. chim. 12, 172; Costa, J. 1891, 336); magnetic rotation (Perkin, Chem. Soc. Trans. 55, 701); crit. temp. 291·2°; crit. density 0·2401 (Ter-Gazarian, J. Chim. Phys. 1906, 4, 140).

From Ba(C₂H₅SO₄)₃ and KCN (Pelouze, Annalen, 10, 249), from cyanogen chloride and Zn(C₂H₅)₂ (Gal, Zeitsch. Chem. 1868, 252), from Zn(C₂H₅)₂ and (CN)₂ (Frankland and Graham, Chem. Soc. Trans. 37, 740), from propionamide and P₂O₅ (Dumas, Malaguti and Leblanc, Annalen, 74, 329). By heating ethyl *isocyanide* to 240° (Nef, *ibid.* 280, 296).

Preparation.—By heating C₂H₅I with pure KCN and alcohol to 180°; C₂H₅Cl dissolved in three times its weight of alcohol is heated with KCN to 100° or 150° (Rossi, Annalen, 159, 79). C₂H₅I is heated with KCN in closed tubes to 180°, and the product distilled, and the distillate is freed from excess of C₂H₅I by means of a solution of CaCl₂, upon which the C₂H₅CN swims, while the heavier C₂H₅I sinks to the bottom (Williamson, Phil. Mag. [4] 2, 205; Gauthier, Ann. Chim. Phys. [4] 17, 180).

It is a mobile colourless liquid with an agreeable odour, soluble in water, from which CaCl₂ or NaCl causes it to separate; miscibility with water (Rothmund, Zeitsch. physikal. Chem. 26, 453); V.D. 1·928. It combines with the hydracids, e.g. HCl; the product C₂H₅NHCl forms monoclinic prisms soluble in water and melting at 121° (Gauthier). HCl gas passed into a well-cooled solution of the cyanide in acetic acid gives acetyl chloride and C₂H₅CONH₂,HCl (Colson, Bull. Soc. chim. [3] 17, 57). Chlorine combines with C₂H₅N to form dichloropropionitrile CH₃·CCl₂·CN, a liquid body, b.p 103°–107°, which polymerises on standing to a solid (C₃H₃(Cl₂N)₃. Propionitrile also forms compounds with metallic chlorides and with cyanogen chloride. C₂H₅N·CNCl is a liquid decomposed by water; b.p. 60°–68° (Hencke, Annalen, 106, 280). Compounds with AlCl₃ (v. Perrier, Compt. rend. 1895, 120, 1423). Propionitrile is hydrolysed by acids or alkalis yielding propionic acid; electrolytic reduction yields* n-propylamine (Ahrens, Zeitsch. Elektrochem 1896, 3, 99). By the action of metallic sodium, polymerisation ensues, the products being sodium cyanide, ethane, and α-iminopropionylethyl cyanide (Meyer, J. pr. Chem. [2] 38, 326; 45, 63).

Ethyl isocyanide, Ethyl carbylamine C₂H₅N : C; b.p. 79°; sp.gr. 0·759 at 4°, 0·7150 at 44·5° (Gauthier, Ann. Chim. Phys. [4] 17, 233); molecular refraction 16·26 (Costa, Gazz. chim. ital. 22, i. 104). By the interaction 'of C₂H₅I and AgCN (Gauthier, Annalen, 151, 239); by distilling KCN with KC₂H₅SO₄, propionitrile also being formed; by digesting ethylamine with chloroform and alcoholic potash (Hofmann, *ibid.* 147, 107).

It is a colourless liquid having a very repulsive smell. It is transformed into propionitrile by heating at 240°; by heating with alcoholic H₂S ethylthioformamide is produced; with sulphur and CS₂ ethylthiocarbimide; combines with CNCl; with C₂H₇Cl at −10° yields C₂H₅N(Cl)O·C₂H₅ (Nef, *ibid.* 280, 296). HgO oxidises it to C₂H₅N : C : O. Yields a chloride C₂H₅N : CCl₂, by treatment with SO₂Cl in ether at −15°; an oil, b.p. 102° (Nef, l.c.). Yields a bromide, C₂H₅N : CBr₂, with bromine in CHCl₃. This gives ethylamine dibromide with water, ethyl *isocyanide* dibromide hydrobromide and ethylthiocarbimide with H₂S, ethyl *iso*cyanide dibromide hydrochloride with dry HCl, an oily ethniodide with ethyl iodide, and diphenylethylguanidine with aniline (Guillimand, Bull. Soc. chim. 1904, iii. 31, 605; 1905, iii. 33, 652). Compounds with cobaltous, ferrous, and ferric chlorides (v. Hofmann and Bugge, Ber. 1907, 40, 3759). (For further reactions, v. Nef, l.c.)

Ethyl derivatives of cyanuric acid. Although cyanuric acid exists in only one modification, probably the *iso*-(II.) esters derived from the tautomeric forms (I. and II.) are known.

$$
\text{I.} \quad
\underset{\substack{\text{C·OH}\\\text{Normal.}}}{
\overset{\text{N}}{
\begin{array}{c}
\text{HO·C} \quad \text{C·OH}\\
\| \quad \quad \|\\
\text{N} \quad \text{N}
\end{array}}}
\qquad
\text{II.} \quad
\underset{\substack{\text{C:O}\\\text{Iso.}}}{
\overset{\text{N·H}}{
\begin{array}{c}
\text{O:C} \quad \text{C:O}\\
| \quad \quad |\\
\text{H.N} \quad \text{N.H}
\end{array}}}
$$
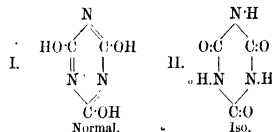
Ethyl cyanurate (C₂H₅OCN)₃; m.p. 29°, b.p. 275° (Claesson, J. pr. Chem. [2] 33, 131). By action of CNCl on C₂H₅ONa (Hofmann, Ber. 19, 2061); also from C₂H₅ONa (3 mols.) and trimethyl cyanurate (H); from CNI or CNBr and C₂H₅I (Ponomarew, Bull. Soc. chim. [1.] 41, 315); by heating the lead salt of the diethyl ester (P.); together with ethyl *iso*cyanurate by treating silver cyanurate with C₂H₅I (C., P.); from di-potassium cyanurate and C₂H₅I (P.).

Only liquid readily soluble in alcohol, ether, CHCl₃ and CS₂, sparingly so in water. Converted into ethyl *isocyanurate by long heating at 180°–200°; yields cyanuric acid with HCl, cyanuric chloride with PCl₅, melamine with strong ammonia and the diethyl ester with baryta water.

Diethyl cyanurate, Diethylcyanuric acid HO(CN)₃(C₂H₅)₂ (Ponomarew, Ber. 18, 3267; Hofmann, *ibid.* 19, 2077). By warming ethyl cyanurate with concentrated baryta water; by treating methyl cyanurate or mono-potassium cyanurate with C₂H₅I.

Thick plates from water, insoluble in ether, sparingly soluble in alcohol. Decomposes on heating into diethyl, *iso*cyanurate; yields cyanuric acid on warming with HCl. Pb salt and C₂H₅I yield triethyl cyanurate, but if C₂H₅I contains free I, triethyl *isocyanurate also formed.

Ethyl isocyanurate, •Triethylcarbimide (C₂H₅NCO)₃. m.p. 95°; b.p. 276°; absorption spectrum (Hartley, Dobbie and Walker, Chem. Soc. Trans. 1901, 849); heat of formation (Lemoult, Compt. rend. 125, 869). By polymerisation of C₂H₅NCO (H. D! and W.); also from potassium cyanate or cyanurate, or from

Pb salt of the diethyl ester and KC_2H_5SO ; by heating ethyl cyanurate at 180°-200° ; together with ethyl cyanurate from silver cyanurate and C_2H_5I (Habich and Limpricht, Annalen, 109, 102).

Rhombic prisms (Rammelsberg, J. 1857, 273 ; Foek, Ber. 19, 2076) moderately soluble in hot water, 'readily so in alcohol. KOH yields $N(C_2H_5)H_2$ and K_2CO_3.

Diethyl isocyanurate, Diethylcyanuric acid $H(NCO)_3(C_2H_5)_2$, m.p. 173°. Obtained in preparing the triethyl ester (Habich and Limpricht, *l.c.*) ; together with cyanuric acid by heating anhydrous mono-potassium cyanurate with C_2H_5I at 170°-180° (Ponomarew, Ber. 18, 3270) ; by heating diethyl cyanurate (Hofmann, *ibid.* 19, 2078).

Hexagonal columns, readily soluble in hot water, alcohol, and ether, sparingly so in cold water. Yields CO_2 and $N(C_2H_5)H_3$ by heating in a sealed tube at 100°. Pb salt and C_2H_5I yield ethyl *iso*cyanurate.

Ethyl diketobutyrate *v.* KETONES.

Ethyl ferrocyanide $(C_2H_5)_4Fe(CN)_6$. From $Ag_4Fe(CN)_6$ and C_2H_5I (Freund, Ber. 21, 935). Rhombic crystals from $CHCl_3$, easily soluble in water and alcohol, insoluble in ether, ligroin, and CS_2. Decomposed at 212°-214°, with formation of ethyl *iso*cyanide. The aqueous solution gives a deep violet tint with $FeCl_3$, and a white precipitate with $HgCl_2$. Molecular weight by cryoscopic method indicates the monomolecular formula (Buchbock, Zeitsch. physikal. Chem. 23, 157).

Ethyl fluoride C_2H_5F. Obtained impure by action of CaF_2 and H_2SO_4 upon C_2H_5OH (Reinsch, J. pr. Chem. 1840, 19, 314) ; by heating $KC_2H_5SO_4$ and $KF·HF$ (Fremy, Compt. rend. 1854, 38, 393). Prepared pure from AgF and C_2H_5I (Moissan, Ann. Chim. Phys. 1890, [6] 19, 272) Colourless gas with ethereal odour, liquefying at −32° under atmospheric pressure. Burns in air with a blue flame. Readily soluble in C_2H_5Br, C_2H_5I, C_2H_5OH, and ether. Decomposed at 100° by heating with KOH in a sealed tube into KF, C_2H_5OH, and ether.

Ethyl formamide $H·CONHC_2H_5$; b.p. 199° ; sp.gr. 0·952 at 21°. By distilling an aqueous solution of $H·COONH_3(C_2H_5)$; separates from distillate upon addition of KOH (Linnemann). By action of $NH_2(C_2H_5)$ upon $CCl_3·CHO$ (Hofmann, Ber. 5, 247) ; a thick colourless liquid.

Ethyl formate $H·CO_2C_2H_5$; b.p. 54·4° at 760 mm., sp.gr. 0·9376 at 0°/4° ; b.p. 53·4°-53.6° at 754·4 mm., sp.gr. 0·8731 at 53·4°/4° (R. Schiff, Annalen, 220, 106) ; b.p. at 760 mm. 54·3°, sp.gr. 0·9480 at 0°/4° ; critical temperature, 235·3° ; critical pressure, 35,550 mm. (Young and Thomas, Chem. Soc. Trans. 1893, 1193). Capillarity constant at boiling-point, a^2 = 4·528 (Schiff, Annalen, 223, 75) ; H.C. p. 388 cals. (Berthelot, Ogier), 391·7 (Delépine).

By distilling a mixture of 6 parts alcohol (90 p.c.), 7 parts sodium formate and 10 parts (conc.) H_2SO_4 (Liebig) ; by distilling a mixture of ethyl oxalate with oxalic acid (Löwig, J. 1861, 599) ; by heating a mixture of glycerol, oxalic acid, and alcohol in a reflux condenser, and then distilling (Lorin, Bull. Soc. chim. [ii.] 5, 12). On the large scale a mixture of 9 parts of starch and 29 parts of MnO_2 (of 85 p.c.) is heated with 28

parts of H_2SO_4, 5 parts H_2O, and 15 parts of alcohol (85 p.c.) (Stinde, Dingl. poly. J. 181, 402).

A mobile colourless liquid with a pleasant aromatic smell ; is used for flavouring arrack and rum ; is decomposed by water, for which it has strong affinity. Sodium in absolute ether decomposes it into CO_2H and C_2H_5ONa (Freer and Sherman, Amer. Chem. J. 18, 581). Cl forms with it in sunlight *dichlorethyl formate* $H·CO_2C_2H_5Cl_2$, a colourless oily liquid, decomposed on heating, and which by action of alkalis is decomposed into acetic, formic, and hydrochloric acids. By further action of Cl in sunlight, *perchlorethyl formate* $Cl·CO_2C_2Cl_5$, b.p. 200°, sp.gr. 1·705 at 18°, is formed (Cloëz, Ann. Chim. Phys. [3] 17, 297)

Ethyl hydrate *v.* ALCOHOL.

Ethyl hydride, Ethane, *Dimethyl* C_2H_6 (Frankland and Kolbe, Chem. Soc. Trans. 1, 60) ; m.p. −171·4° ; b.p. at 749 mm. −85·4° (Ladenburg and Krügel, Ber. 32, 1821), −172·4° and −84·1° (Cardoso and Bell, J. Chim. Phys. 1912, 10, 497), −88·5° (Maass and McIntosh, J. Amer. Chem. Soc. 1914, 36, 737), −89·3° (Burrell and Robertson). Gas : sp.gr. 1·036, condensed at 4° and 46 atmospheres pressure (Cailletet, J. 1877, 68) ; critical constants (*v.* Hainlen, Annalen, 282, 245 ; Olszewski, Ber. 1894, 27, 3306 ; and Keunen, Chem. Zentr. 1897, ii. 540 ; Cardoso and Bell, *l.c.*) ; heat of vaporisation $14·6+10^{10}$ ergs per mol. ; density at the b p. 0·5490 (Maass and McIntosh, *l.c.*) ; sol. in water at $t°$

$$(1) \quad \frac{9·4556 - 0·35324t + 0·006278t^2}{100}$$

$$(2) \quad \frac{8·710 - 0·33242t + 0·00603t^2}{100}$$

(1) Schockendants (Annalen, 109, 116), (2) Bunsen (Gasometry). Sol in alcohol=1·5 (Berthelot, J. 1867, 344) ; H.C. p. 373·3 Cals. (Th.)=372·3 (Berthelot, Ann. Chim. Phys. [6] 30, 559) ; H.F. (from amorphous C)=11·7 Cals. (B.) ; occurs in crude petroleum.

Pittsburg gas consists of ethane mixed with a little CH_4 and CO_2, and is used for smelting and lighting purposes.

By action of K upon C_2H_5CN, also by action of water upon $Zn(C_2H_5)_2$ (Frankland and Kolbe, Chem. Soc. Trans. 3, 338) ; by action of Zn upon C_2H_5I in presence of water ; by electrolysis of acetic acid or acetates (Kolbe, Annalen, 69, 279) ; by heating 9 parts of C_2H_5I with 2·6 parts of $AlCl_3$ to 140° or 150° (Köhnlein, Ber. 16 562) ; by action of $Hg(C_2H_5)_2$ upon H_2SO_4 (Schorlemmer, Annalen, 132, 234) ; by heating an excess of BaO_2 with acetic anhydride and sand (Schützenberger, Zeitsch. Chem. 1865, 703 ; Darling, Annalen, 150, 216) ; by the action of nascent H (from ZnCu couple or Zn dust) upon a mixture of C_2H_5I and C_2H_5OH (Sabanejeff, Ber. 9, 810). By combining C_2H_4 or C_2H_5 with H in presence of reduced Ni (Sabatier and Senderens, Compt. rend. 124, 1360 ; 128, 1173). Ethane is now produced on an industrial scale by means of this reaction carried out under pressure. For details of the process, *see* Sprent (J. Soc. Chem. Ind. 1913, 171). From EtI and potassium hydride in sealed tubes at 180°-200° (Moissan, *ibid.* 134, 389). Reduced Ni at 395° breaks ethane up into C and C_2H_4 (Berthelot).

Ethyl iodide C_2H_5I (Gay-Lussac, Ann. Chim. Phys. [1] 91, 89 ; Serullas, *ibid.* [2] 25, 323 and 42, 119 ; Frankland, Chem. Soc. Trans. 2, 263 ; 3, 32) ; m.p. −118° (Schneider) ; b.p. 72·34° (Linnemann, Annalen, 160, 204), b.p. 71·3° (Andrews), 72·57° (corr.) (Thorpe and Rodger), 71·9°−72° (Linebarger) ; sp.gr. 1·9444 at 14·5° (L.), 1·9755 at 0° (Pierre), 1·9309 at 15° (Mende-léeff), sp.gr. 1·1810 at 72·2°/4° (Schiff), sp.gr. 1·9053 at 4°, 1·9433 at 15°, 1·9243 at 25° (Perkin) ; V.D. 5·417 (Marchand).

From alcohol and HI (Gay-Lussac) ; from alcohol, iodine, and phosphorus (Serullas). Per-sonne (Compt. rend. 42, 468) suggested the use of red P, and, according to Beilstein (Annalen, 126, 250), 1 part red P and 5 parts of alcohol (90 p.c.) are placed in a retort, and 10 parts of iodine slowly added. After 24 hours the C_2H_5I is distilled off, washed with NaOH solution and with water, and dried over $CaCl_2$. Crismer (Ber. 1884, 649) dissolves 1 in liquid paraffin adds yellow P and then alcohol. Walker (Chem. Soc. Trans. 1892, 717 ; *cf. ibid.* 1905, 1596) obtained a 93 p.c. yield from alcohol, iodine, and equal parts of red and yellow phos-phorus (*cf.* Adams and Voorhees, J. Amer. Chem. Soc. 1919, 41, 789). Prepared in quantitative yield by adding Et_2SO_4 slowly to a warm con-centrated aqueous solution of KI (Weinland and Schmid, D. R. P. 175209). Also from action of HI upon ether (Cottrel Rogers), and together with iodoform and NaI by electrolysis of a solu-tion of 20 grams C_2H_5COONa, and 20 grams KI in 20 c.c. of water (Miller, Hofer, and Reindel).

C_2H_5I is a colourless, pleasantly smelling liquid, almost insoluble in water, but miscible with alcohol and ether. It precipitates silver from its solutions in the cold, easily forms double compounds with silver salts, metals, and am-monia. Br displaces the I, and forms C_2H_5Br ; Cl forms C_2H_5Cl (Dumas, Stas, Annalen, 35, 162) ; ICl forms C_2H_5Cl and I_2. HCl has no action, but, on the contrary, C_2H_5Cl is decom-posed by HI into C_2H_5I and HCl (Lieben, Zeitsch Chem 1868, 712). By action of KI at 150°, ethane and iodine are formed. HNO_3 also causes the separation of I (Marchand, J. pr. Chem 1884, 33, 186). Metallic Ag abstracts I, and leaves butane (C_4H_{10}) By heating with water to 150°, we get alcohol (Reynoso, J. 1856, 567) ; with excess of alcohol yields ether and some C_2H_4 (Lieben, Rossi, Annalen, 158, 166). Is gradually turned brown by exposure to light, owing to formation of free I and liberation of butane (Frankland, Chem. Soc. Trans. 3, 322). In presence of mercury the reaction is much more rapid, owing to combination of the liberated I with Hg. Is used largely for the preparation of other ethyl compounds.

Ethyl nitrate $C_2H_5\cdot O\cdot NO_2$, *Nitric ether* ; m.p. −112° (Schneider) ; b.p. 86·3° at 728·4 mm. ; sp.gr. 1·1322 at 0°, 1·1123 at 15·5° (Kopp, Annalen, 98, 367) ; b.p. 87·6° ; sp.gr. 1 1305 at 4°, 1·1159 at 15°, 1·1044 at 25° (Perkin) ; H.F.p. = 40,870 ; H.F.v. = 38,750 ; H.C. = 325, 690 (Th. 4, 214). Obtained from alcohol by the action of nitric acid in presence of some substance which will destroy nitrous acid, *e.g.* urea (Millon, Ann. Chim. Phys. [3] 8, 233).

Preparation.—400 grams of pure nitric acid (sp.gr. 1·40) previously heated with 1 p.c. of urea in order to destroy lower oxides of nitrogen)

are mixed with 300 grams absolute alcohol and 100 grams of urea nitrate, and distilled ; when half the liquid has distilled off, a mixture of 400 grams of nitric acid and 300 grams of alcohol is allowed to drop into the retort and the distil-lation continued (Lossen, Annalen, Suppl. 6, 220).

Silver nitrate, heated with ethyl iodide (or bromide) and alcohol, yields, not ethyl nitrate, but the nitrite, together with aldehyde (Bertrand, Bull. Soc. chim. 33, [ii.] 566). If, however, EtI be added gradually to powdered $AgNO_3$, kept cool, a theoretical yield of $EtNO_3$ is formed (Von Biron, J. Russ. Phys. Chem. Soc. 30, 667).

Ethyl nitrate is a colourless liquid with pleasant odour and taste ; almost insoluble in water, but miscible with alcohol and ether. Ammonia forms ethylamine nitrate ; nascent hydrogen yields hydroxylamine and other bases (Lossen). Sulphuretted hydrogen yields mer-captan (Kopp, Annalen, 64, 320). Alcoholic potash decomposes it with separation of crystals of potassium nitrate.

Ethyl nitrite $C_2H_5\cdot O\cdot NO$, *Nitrous ether* ; b.p. 16·4° (Liebig), 17° (Mohr, J. 1854, 561 ; Brown, Pharm. J. 15, 400), 17·5° (Dunstan and Dy-mond, *ibid.* 18, 861) ; sp.gr. 0·900 at 15·5° (Br.) ; 0 917 at 0°/0° (D. and D.) ; H.F.p. = 30,610 ; H.F.v. = 28,870 (Th. 4, 217).

This body was discovered in 1681 by Kunckel. Obtained from alcohol by action of nitric acid, especially in presence of some oxidisable matter, *e.g.* copper.

Preparation.—500 grams of potassium nitrite and 1 litre alcohol (45 p.c.) are mixed and cooled by means of ice ; a mixture of sulphuric acid (500 grams), water (500 grams), and alcohol (500 grams) is then slowly dropped in, the heat produced volatilises the ether, which is con-densed in an efficient condenser (Feldhaus, Annalen, 126, 71). Dunstan and Dymond (*l.c.*) recommend that 34·5 grams sodium nitrite in 120 grams water be slowly mixed with a mixture of 13·5 grams of sulphuric acid with 32 grams alcohol and about 75 c c. water kept cool by ice. The ethyl nitrite separates out as a layer floating on the surface. As thus prepared, the liquid contains only traces of alcohol, from which it is freed by shaking with water. Alkali ethyl sulphates react with alkali nitrites, yielding nitrous ester and nitroethane (Ray and Neogi, Chem. Soc. Trans. 1906, 1900). Also formed by the interaction of $MgSO_4$, $NaNO_2$, and C_2H_5OH (Matuschek, Chem. Zeit. 1905, 29, 115).

Ethyl nitrite is a mobile liquid with a plea-sant ethereal smell and taste, liable to undergo decomposition, especially in presence of water. It can be preserved if mixed with alcohol and a small quantity of glycerol. It is decomposed by sulphides in accordance with the following equation :

$$C_2H_5NO_2 + 3H_2S = NH_3 + C_2H_6O + H_2O + 3S$$

(Kopp, Annalen, 64, 321).
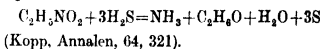
It is slightly soluble in water and miscible with alcohol. Mixed with alcohol it constitutes the ' sweet spirit of nitre,' *spiritus ætheris nitrosi*, of the British Pharmacopœia, which is thus pre-pared : To 4000 millilitres of alcohol (90 p.c.) add gradually 100 millilitres of sulphuric acid, and then 125 millilitres of nitric acid, stirring constantly. Transfer the mixture to a retort or

flask, in which 100 grams of copper in fragments have been placed, and to which is attached an efficient condenser with a receiver containing 1000 millilitres of 90 p.c. alcohol. Surround the receiver with ice-cold water and distil gently at a temperature which is at first about 77°, and rises to 80°, but does not exceed 82°, until the volume of liquid in the receiver has been increased to 1600 millilitres. Then allow the contents of the retort to cool. add 25 millilitres of nitric acid, and resume the distillation until the liquid in the receiver is increased to 1700 millilitres. Mix this liquid with 1000 millilitres of the alcohol so as to make the whole contain 2·66 p.c. of ethyl nitrite.

Ethyl oxalylsuccinate v. KETONES.

Ethyl oxide $(C_2H_5)_2O$, **Ether**, *Ethyl ether*, *Vinic ether*; formerly called *Sulphuric ether*, *Phosphoric ether*, &c., according to the acid used in its preparation ; m.p. $-117 \cdot 6°$ (Archbald and McIntosh), m p. $-112 \cdot 6°$ (Ladenburg, and Krugel) ; b.p, $34 \cdot 97°$ (Regnault), $34 \cdot 6°$ at 762 mm.ₐ (Schiff, Annalen, 220, 332), $34 \cdot 9°$ (Kopp) ; sp.gr. 0·7360 at 0°, 0·7185 at 17·5° (Hager), 0·6950 at 34·6°/4° (Schiff), 0·7024 at 15°, 0·7099 at 25°/25°, 0·7201 at 15°/15° (Perkin, Chem. Soc. Trans. 45, 474), sp.gr. 0·71982 at 15°/15° (Wade and Finnemore), sp.gr. 0·7183 at 17·1° (Brühl), sp.gr. 0 70942 at 25° (Linebarger) ; M.M. = 4 777 at 20° . freezes at −129° to a crystalline mass, which melts at −117·4° (Olzewski, Monatsh. 5, 128) ; capillarity constant at b.p. $a^2 = 4 \cdot 521$ (Schiff) ; fl. at 17·5° = 8 ; critical temperature, 194° ; critical pressure, 35·61 atmospheres (Ramsay and Young). ·Vapour tension 67·49 mm. at −23°; 182·34 mm. at 0° ; 286·4 mm. at 10° ; 433·2 at 20° ; 636·3 at 30°.

The preparation of ether from alcohol and sulphuric acid was first described by Valerius Cordus (1540), and the method of making this ' oleum vitroli dulce ' was published in 1552 by Conrad Gessner. Frobenius, 1730, named it sulphuric ether. Val. Rose (Scher. J. 4, 253) showed that it contained no sulphur, but its composition was first made out by Saussure and also by Dumas and Boullay (Ann. Chim. Phys. [2] 36, 294). Its constitution was first studied by Liebig (Annalen, 60, 31 ; 23, 39) and Regnault (Ann. Chim. Phys. [2] 71, 352). Williamson, in 1850-51 (B. A. 1850, 65, and Phil. Mag. [3] 37, 350), established the views now held as to its constitution and formation.

Formation.—From alcohol, by action of phosphoric or arsenic acid (Boullay) ; by action of boron fluoride (Desfosses, Ann. Chim. Phys. [2] 36, 294) ; of $ZnCl_2$ (Masson, Annalen, 31, 63) ; of $SnCl_4$, and other metallic chlorides (Kühlmann, *ibid.* 33, 97, 192). From alcohol by heating with dry NH_4Cl to 260°-400° (Berthelot, Annalen, 83, 110). From C_2H_5NaO and C_2H_5I (Williamson). From alcohol and HCl, HBr, or HI at 200° or 240°, or by heating alcohol with $ZnCl_2$, $SnCl_4$, $CaCl_2$, $MgSO_4$, or chrome alum to 300° (Reynoso, Ann. Chim. Phys. [3] 48, 385). Also from C_2H_5Br or C_2H_5I and HgO (Reynoso), or from C_2H_5I and Na_2O (Green, Bull. Soc. chim. [ii.] 29, 458).

The continuous method now adopted is due to Boullay (J. Pharm. Chim. 1, 97), and the true explanation of the action was first given by Williamson (*l.c.*). The alcohol and sulphuric acid

first form $C_2H_5HSO_4$ and H_2O, and then, by the action of $C_2H_5HSO_4$ upon more alcohol, $(C_2H_5)_2O$ and H_2SO_4 are formed. That this is true Williamson proved by using amyl sulphuric acid and ethyl alcohol, when amyl-ethyl ether was produced (*cf.* Prunier, J. Pharm. Chim. 1897, 5, 513). Addition of $Al_2(SO_4)_3$ increases rate of production of ether owing to catalytic action (Senderens, Compt. rend. 1910, 151, 392).

Preparation.—Boullay's method is usually employed. A mixture of 9 parts H_2SO_4 with 5 parts of alcohol (90 p.c.) is placed in a retort, and alcohol is slowly dropped in and the temperature is maintained between 130° and 140°. An iron retort lined with lead is usually employed, and the ordinary mercurial thermometer, which is, of course, liable to fracture, is replaced by a bulbed tube containing some non-drying oil. The tube is then either exhausted by the air-pump, and hermetically sealed, or its open end is closed by a plug of cotton wool, and two marks are made on the tube corresponding to positions of the surface of the oil at 130° and 140° respectively. In order to avoid risk of explosion by contact of the vapour with direct flame, coils of lead tubing, conveying superheated steam or the vapour of some liquid of high boiling-point (*e.g.* coal-tar phenol), are used as a source of heat. The distillate is treated with milk of lime or solution of soda in order to remove the SO_2 which is always simultaneously formed. It is then rectified in an apparatus devised by Mohr, which consists of a still from which the vapour is led through a vessel kept at 38° by warm water. Here the alcohol and water vapours are condensed, and the ether passes over, and is condensed in an efficient condenser.

By means of an apparatus devised by Soubeiran, ether can be prepared in a fairly pure state by one operation. A mixture of about 30 lbs. of H_2SO_4 with 20 lbs. of alcohol of 85 p.c. is heated rapidly to 130° in a copper still, to the bottom of which two tubes convey alcohol from a tinned copper reservoir. The neck of the retort (which is of lead) is connected with the first condenser, which is a copper vessel kept warm by allowing the waste water from the worm tub (where the ether is condensed) to flow over the outside of it. Here the steam and vapour of alcohol are condensed, and the liquid formed can be drawn off from below by means of a stopcock. The ether vapour then passes on to the purifier, which consists of a vessel filled with wood charcoal saturated with a solution of caustic soda, which not only removes the SO_2, but also absorbs the oil of wine. The pure ether passes on, and is condensed in a well-cooled worm. The greatest yield of ether is obtained at 140°-145° ; below this temperature the yield is less, and above this much SO_2 is evolved (Prescott and Norton, Amer. Chem. J. 6, 243). Other apparatus have been described by Annaratone (Fr. Pat. 408089 ; J. Soc. Chem. Ind. 1910, 592), Fritzsche (Zeitsch. anal. Chem. 1897, 36, 298), Barbet et fils et Cie (Fr. Pat. 479435, 1914). Sulphuric acid has been largely replaced by benzenesulphonic acid in this preparation (Krafft, Ber. 26, 2831 ; D. R. P. 69115 ; Frdl. iii. 11).

Commercial ether contains water, alcohol, aldehyde, methyl compounds, ketones, and vinyl alcohol. A. J. Jones (Pharm. J. 1919, 103, 71)

found that in commercial samples, methyl compounds range from 0·02 to 0·06 p.c., sp.gr. 0·7182-0·7211, and ketones (as acetone) from 0·09 to 5·0 pts. per 10,000. Vinyl alcohol may be removed by shaking with water or treatment with bromine, phenylhydrazine, or potassium hydroxide (Poleck and Thümmel, Ber. 22, 2863), and the other impurities by treatment with dry $Fe(OH)_2$, prepared from crystallised $FeSO_4$, and an equimolecular weight of powdered lime (Gaborini, Bull. Assoc. Chim. Sucr. Dist. 1909, 26, 1165); by treatment with potassium hydroxide and powdered potassium permanganate, and finally drying with calcium chloride (Fierz; Wade and Finnemore, Chem. Soc. Trans. 1909, 1842; François, Chem. Zentr. 1897, ii. 144; Fritsch, Chem. Zeit. 1909, 33, 759). Phosphorus pentoxide may be substituted for calcium chloride (Lieben, Annalen, Suppl. 7, 218). (For other methods, v Guigues, J. Pharm. Chim. 1906, 24, 204; and Ekenberg, Zeitsch. anal. Chem. 36, 245.)

According to the B.P., 1914, ordinary ether should have a sp.gr. of 0·726, 15°/15°, and boil between 34° and 36°. Purified ether (Æther purificatus of the B.P.) should give no yellow colouration with solid potassium hydroxide in the dark, or with a solution of freshly prepared solution of potassium iodide. To test for presence of methyl compounds shake 2 vols. of the ether with 1 vol. of 20 p.c. alcohol and 1 vol. of water, allow the mixture to separate, and draw off the lower layer. Mix 5 millilitres of this lower layer with 2·5 millimetres of an aqueous solution (1 in 50) of potassium permanganate and 0·2 millilitre of sulphuric acid. At the end of 3 minutes add 0·5 millilitre of an aqueous solution (9·6 in 100) of oxalic acid, followed by 1 millilitre of sulphuric acid, and then by 5 millilitres of decolourised solution of fuchsin, and mix thoroughly. No violet colour should be produced within 20 minutes.

Wade and Finnemore (l.c.) find that ether and water form a binary mixture, b.p. 34·15°, containing 1·3 p.c. water, and that slight traces of alcohol greatly increase the solubility of water in ether. 1 gram ether dissolves 0·023 gram water at 15°–20° and 0·019 at 10° (cf. Schunke, Zeitsch. physikal. Chem. 14, 331; Napier, Bull. Soc. chim. 29 [ii.] 129); 1 gram water absorbs at 0°, 0·12465; at 10°, 0·09599; at 20°, 0·07487; at 30°, 0·06370 gram ether (Schunke, l.c.; Tolloczko, Ber. 28, 808; Klobbie, Zeitsch. physikal. Chem. 24, 615; Osaka, J. Soc. Chem. Ind. 1909, 625). If ether be shaken with an equal volume of CS_2, a turbidity is produced if water be present. A better test is with anhydrous copper sulphate or amalgamated aluminium.

Decompositions.—Pt black, CrO_3 or HNO_3 oxidise ether to acetic acid; ozone produces ethyl peroxide. Ether vapour and air at 100°, in the presence of a copper catalyser and platinum-black, yield acetaldehyde and formaldehyde (Orlow, J. Russ. Phys. Chem. Soc. 1908, 40, 799; cf. Legler, Annalen, 217, 392). When ozonised oxygen is passed into ether, a solution is obtained containing $C_2H_6O_4$, $C_2H_6O_2$, and H_2O_2, also a small quantity of CH_2O_2 (A. W. Wright). Ether combines with H_2SO_4 to form $C_2H_6HSO_4$; by action of SO_3 we first get $(C_2H_5)_2SO_4$, but by excess of SO_3, $C_2H_4HS_2O_7$ and a small quantity

of a body of the composition $CH_2(SO_3C_2H_5)_2$ are formed. When ether is heated with water and a small quantity of H_2SO_4 to 150°-180°, alcohol is formed (Erlenmeyer, Zeitsch. Chem. 1868, 343). According to Lieben (Annalen, 165, 136), the reaction goes on, though very slowly, without H_2SO_4, and at the ordinary temperature. Ether combines easily with HI and yields C_2H_5I (Silva, Ber. 8, 903), and is decomposed by heating with zinc-dust into C_2H_4 and water (Jahn, Monatsh. 1, 675); bromine and aqueous ether yield bromacetaldehyde (Maugin, Compt. rend. 1908, 147, 747).

Instances of the spontaneous explosion of ether on heating are not unknown, due probably to the presence of ethyl peroxide produced by autoxidation. Ether occasionally contains hydrogen peroxide and acetaldehyde and a relatively large amount of vinyl alcohol (Kassner, Arch. Pharm. 1912, 250, 436). Hydrogen peroxide may be detected by the immediate red colouration produced when 5 c.c. is treated with 1 c.c of $N/10$ potassium thiocyanate solution and 2 drops of a 5 p.c. freshly prepared acidified solution of ferrous ammonium sulphate (Dietze, Apoth. Zeit. 1915, 30, 165). There should be no liberation of iodine when 2 c.c. of a 10 p.c. solution of cadmium potassium iodide are shaken with 10 c.c. of the sample. Peroxides or peroxidised compounds may be formed in ether when improperly stored. The degree of oxidation is dependent upon the nature of the container, the purity of the ether, the amount of air present, and, in the case of glass containers, the intensity of the light which accelerates the oxidation. Peroxides may be removed by means of ferrous hydroxide or by shaking with mercury.

Mixtures of ether vapour and air explode when heated to about 190° if the amount of ether in the gaseous mixture reaches 1 gram per litre.

A hydrate $(C_2H_5)_2O,2H_2O$ is known; it is a solid body, which only exists below $-3\cdot5°$, and is obtained by the rapid evaporation of aqueous ether on filter paper (Tanret, Bull. Soc. chim. 30, 505; Compt. rend 87, 765). Dry ether and chlorine at $-80°$ yield a white crystalline chloride $(C_2H_5)_2OCl_2$, m.p. $-51°$; bromine similarly yields a reddish-yellow bromide $(C_2H_5)_2OBr_2$, m.p. $-40°$ (McIntosh, Chem. Soc. Trans. 1905, 789). A bromide $(C_2H_5)_2OBr_2$, red plates, m.p. 22°, is also known (Schutzenberger, Annalen, 167, 86).

Ether combines with various metallic salts and forms crystalline bodies, e.g. $BeCl_2$, $2(C_2H_5)_2O$, large prisms (Atterberg, Ber. 9, 856); $HgBr_2,3(C_2H_5)_2O$ (Nicklès, J. 1861, 200); $AlBr_3,(C_2H_5)_2O$ (N.). $TiCl_4(C_2H_5)_2O$; crystalline; m.p. 42°-45°; b.p. 118°-120°, decomposes into $TiCl_2(OC_2H_5)$ (Bedson, Annalen, 180, 236; Chem. Soc. Trans. 1876, 1, 311).

Properties.—A colourless mobile liquid with pleasant smell. Volatilises very quickly, and by so doing produces great cold. It is extremely inflammable, and its vapour, which is very heavy, forms an explosive mixture with air. Ether is readily soluble in concentrated HCl solution (Dräper, Chem. News, 35, 87), and in concentrated H_2SO_4, from which it is separated by addition of ice (Riedel, D. R. P. 52982, Frdl. ii. 551). It is miscible with almost all

organic liquids, and with liquid CO_2. It is a good solvent for resins, fats, alkaloids, &c., and sulphur and phosphorus dissolve in it to a small extent. It also dissolves I and many salts, e.g. Fe_2Cl_6, $HgCl_2$, $PtCl_4$, and many gases, notably ammonia.

In laboratories ether should always be kept over mercury or sodium in completely filled, well-stoppered bottles, preferably made of blue, green, or brown.glass, in cool places excluded from the. light (cf. Baskerville and Hamor, J. Ind. Eng. Chem. 1911, 3, 301 et seq.; J. Soc. Chem. Ind. 1911, 830).

Its vapour when inhaled produces insensibility (Faraday, 1818), and it is used as an anæsthetic in surgery. It is also occasionally used in surgery for producing local anæsthesia; this is done by directing a spray of ether upon the skin, when the extreme cold produced by evaporation produces complete insensibility.

It is also used as a solvent in the preparation of collodion, in the extraction of tannic acids, of several alkaloids, &c.

Chlorine acts v olently upon ether, setting fire to it, and liberating carbon (Cruikshank) If the ether be kept cool by ice, and in the dark, substitution products are obtained. The Cl replaces the H atom by atom from one ethyl group first, in the following order: $CHHHCHHOC_2H_5$

$$\begin{array}{ccccc} & 2 & 3\ 4 & 1 & 5 \end{array}$$

(Liebou, Annalen, 111, 121; 146, 180; Abeljanz, 164, 197; Jacobsen. Ber. 4, 215; also Liebig, Annalen, 1, 220; Malaguti, Ann. Chim. Phys. [2] 70, 338; [3] 16, 5; Fritsch and Schumacher, Annalen, 279, 302).

Monochlorether, *Monochlorethyl oxide*

$CH_3 \cdot CHCl \cdot O \cdot C_2H_5$;
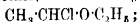
b p. 97°-98°; by the chlorination of ether (Lieben); by saturating a mixture of aldehyde and alcohol with HCl (Frapolli, Wurtz, Annalen, 108, 226); by the action of PCl_5 upon acetal (Bachmann, ibid. 218, 39). It is decomposed by H_2SO_4 into HCl, C_2H_4O, and $C_2H_5 \cdot OH$. C_2H_5ONa forms NaCl and acetal; water decomposes it into HCl, aldehyde, and alcohol (Laatsch, Annalen. 218, 36).

Dichlorether, *Dichlorethyl oxide*

$CH_2Cl \cdot CHCl \cdot O \cdot C_2H_5$;

b.p. 140°-145°; sp.gr. 1·174 at 23°; by action of Cl upon ether (Malaguti, Annalen, 32, 15; Wildman and Gray, J. Amer. Chem. Soc. 1919, 41, 1122); by action of HCl upon a mixture of chloraldehyde and $C_2H_5 \cdot OH$ (Natterer, Monatsh. 5, 496); by action of HCl upon chloracetal (N.).

Dichlorether is decomposed on heating in a tube into C_2H_5Cl and other products. C_2H_5ONa forms first *chlordacetal* $CH_2Cl \cdot CH(OC_2H_5)_2$. By heating with excess of C_2H_5ONa in sealed tubes, *ethyl glycol acetyl* $CH_2(OC_2H_5)CH(OC_2H_5)_2$ is formed. In ethereal solution, $Zn(C_2H_5)_2$ yields *ethyl chlorether* $CH_2Cl \cdot CH(C_2H_5)OC_2H_5$; b.p. 141°; sp.gr. 0·9735 at 0°. With excess of $Zn(C_2H_5)_2$ we get $CH_2(C_2H_5)CH(C_2H_5)OC_2H_5$; b.p. 131·4° at 749·6 mm.; sp.gr. 0·7865 at 0° (Lieben, Annalen, 178, 14). Strong caustic potash forms alcohol, a body $C_8H_{16}Cl_2O_3$, a little glycollic acid, and two isomeric bodies of the composition $C_4H_9ClO_2$ (Abeljanz, ibid. 164, 218): α-$C_4H_9ClO_2$, *chloraldehyde alcoholate* $CH_2Cl \cdot CH(OH)O \cdot C_2H_5$, b.p. 93°-95°; and β-$C_4H_9ClO_2$ *oxychlorether* $CH_2OH \cdot CHCl \cdot O \cdot C_2H_5$,

also formed by chlorination of ether (Jacobsen, Ber. 4, 217), b.p. 151°-155°. With $NH_3 \cdot OH$ yields glyoxime (Hantzsch and Wild, Annalen, 289, 293). It is decomposed by water, and in presence of marble yields monochloracetaldehyde alcoholate, which, on distillation, gives monochloraldehyde and monochloracetal (Fritsch and Schumacher, ibid. 279, 301).

Trichlorether $CHCl_2 \cdot CHCl \cdot O \cdot C_2H_5$; b.p. 167°-168°, 155°-158° (Copaux), 170°-175° (Oddo and Mameli); sp.gr. 1·3303 at 14° (O. and M.). By the action of PCl_5 upon dichloracetal $CHCl_2 \cdot CH(OC_2H_5)_2$ (Krey, J. 1876, 475); by hydrolysis of the compound formed by action of chlorine on triethyl boric ester (Copaux, Compt. rend. 127, 721); by chlorinating αβ-dichloroethyl ether with 1 molecule of Cl at temperature of boiling saturated salt solution. At 230°-240° in a sealed tube, yields dichloroaldehyde and C_2H_5Cl. HCl at 110° for 6 hours, and distillation with concentrated H_2SO_4, yield the same products. Conversely, dichloroaldehyde in alcohol with HCl yields trichloroether. Boiled with water, trichloroether yields acetaldehyde, dichloroacetaldehyde hydrate (m.p. 55°-56°, b p. 96·5°-97·5°), dichloroacetal, and other very complex compounds (Oddo and Mameli, Gazz. chim. ital. 33, ii. 373; also ibid. 36, i 480); decomposed by heating with C_2H_5ONa, yielding *dichloracetal*.

Tetrachlorether $CCl_3 \cdot CHCl \cdot O \cdot C_2H_5$; b.p. 189·4° at 749·1 mm., 79° at 16 mm., 189·7° at 758·7 mm.; sp.gr. 1·4225 at 18°/4° (Weber and Foster, J. Amer. Chem. Soc. 31, 1410); sp.gr. 1·4379 at 0°, 1·4182 at 15 2°. Formed by action of Cl upon monochlorether in contact with I (Wurtz, Vogt, Zeitsch. Chem. 1871, 689), or of chloral alcoholate $CCl_3 \cdot CH(OH)O \cdot C_2H_5$ upon PCl_5 (Henry, Ber. 5, 101, 435; Paternò, Pisati, J. 1872, 303). From *trichlorvinyl ethyl ether* and chlorine (Godefroy). A liquid with a camphor-like smell, decomposed by heating with water into C_2H_4OH, HCl, and chloral. Alcoholic KOH forms with it *trichlorvinyl ethyl ether* $CCl_2 : CCl \cdot O \cdot C_2H_5$. Heated with alcohol, forms trichloracetal (Pergami).

Pentachlorether. Two isomerides:
(1) $CCl_3 \cdot CCl_2 \cdot O \cdot C_2H_5$; b.p. 190°-210° with decomposition; sp.gr. 1·645 (Jacobsen, Ber. 4, 217); by action of Cl upon trichlorvinyl ethyl ether (v. supra) (Busch, Ber. 11, 445).
(2) $CCl_3 \cdot CHCl \cdot O \cdot CH_2 \cdot CH_2Cl$; b.p. 235°; sp.gr. 1·577 at 80°. By action of PCl_5 on a compound of chloral and glycol chlorohydrin

$CCl_3 \cdot CH(OH)O \cdot CH_2 \cdot CH_2Cl$
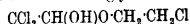
(Henry, Ber. 7, 763).

Hexachlorether $CHCl_2 \cdot CHCl \cdot O \cdot CHCl \cdot CHCl_2$; b.p. 250°; by action of PCl_5 upon dichloraldehyde saturated with HCl (Paternò, Pisati, J. 1871, 508).

Octochlorether $C_4H_2Cl_8O$; from ethylidene oxychloride and Cl in sunlight (Roth, Ber. 8, 1017). Camphor-like smelling, volatile crystals.

Perchlorether $(C_2Cl_5)_2O$ (Regnault, Annalen, 34, 27); sp.gr. 1·900 at 14·5° (Malaguti, Ann. Chim. Phys. [3] 16, 4); the ultimate product of the action of Cl upon ether in sunlight, is a solid, forming orthorhombic scales, m.p. 69°, which possesses a smell like that of camphor. Decomposed by heating at 300° into C_2Cl_6 and $CCl_3 \cdot COCl$; with H_2S yields perchlorvinyl ether

$(C_2Cl_3)_2O$; with liberation of S (Malaguti, Ann. Chim. Phys. [3] 16, 19). This body is a liquid, b.p. 210°, sp.gr. 1·652 at 21°, which combines with Cl in sunlight to form $(C_2Cl_5)_2O$, or with Br yielding $(C_2Cl_3Br_2)_2O$.

Ethyl peroxide $(C_2H_5)_4O_3$, produced by leading dry ozone into absolute ether (Berthelot, Bull. Soc. chim. ii. 36, 72), is a thick syrup which does not solidify at −40°, is partially volatile on heating, but easily explodes ; is miscible with water, by which it is decomposed into C_2H_5OH and H_2O_2.

Ethyl phosphates.

1. *Normal ethyl phosphate* $(C_2H_5)_3PO_4$; b.p. 215° ; sp.gr. 1·072 at 12°. By action of heat on lead diethyl phosphate $Pb(C_2H_5)_4(PO_4)_2$ (Vogeli, Annalen, 69, 190) ; from C_2H_5I and Ag_3PO_4 (Clermont, Ann. Chim. Phys. [3] 42, 330) : from $POCl_3$ and C_2H_5ONa (Lamprecht, Annalen, 134, 347) ; from P_2O_5 and absolute alcohol (Carius, *ibid.* 137, 121). Colourless liquid, miscible with and slowly decomposed by water, forming diethyl phosphoric acid.

2. *Diethyl phosphoric acid* $(C_2H_5)_2HPO_4$, a syrupy liquid obtained by action of P_2O_5 upon alcohol. It is a monobasic acid, and forms well-marked salts, *e.g.* $Ca[(C_2H_5)_2PO_4]_2$, crystalline needles ; $Pb[(C_2H_5)_2PO_4]_2$, needles, m·p. 180°, soluble in water.

3. *Ethyl phosphoric acid* $H_2(C_2H_5)PO_4$, an oily liquid decomposed by heating, evolving $(C_2H_5)_2O$, C_2H_5OH, and C_2H_4. Equal parts of alcohol (95 p.c.) and syrupy H_3PO_4 are heated to 60° or 80°, diluted with water and neutralised with $BaCO_3$, filtered, the Ba salt allowed to crystallise, and then decomposed by H_2SO_4 (Pelouze, Ann. Chim. Phys. [2] 52, 37).

Also produced by action of P_2O_5 upon ether or alcohol or of syrupy H_3PO_4 upon ether (Vögeli, J. 1847-48, 694). Forms crystalline salts with the metals ; of these the lead salt is least soluble.

Ethyl phosphites.

1. *Triethyl phosphite* $(C_2H_5)_3PO_3$; b.p. 191° (or 188° in stream of H) ; sp.gr. 1·075 at 15·5° (Railton, Chem. Soc. Trans. 1855, 7, 216) ; from PCl_3 and alcohol or sodium ethoxide.

An ethereal-smelling liquid, which absorbs O and is converted by PCl_5 into $PO(OC_2H_5)Cl_2$, PCl_3, and C_2H_5Cl (Geuther, Hertz. J. 1876, 207). By heating with $NaOC_2H_5$ yields $Na(C_2H_5)_2PO_3$; with $(C_2H_5O)_2O$, gives

$$H_2(C_2H_5)PO_3$$
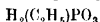
(Jachne, Annalen, 256, 269).

2. *Diethyl-phosphorous acid* $H(C_2H_5)_2PO_3$; b.p. 184°-185° ; sp.gr. 1·0749 (15·5°/4°). From P_4O_6 and C_2H_5OH (Thorpe and North, Chem. Soc. Trans. 1890, 634) ; from PCl_3 and C_2H_5OH (Levitsky, J. Russ. Phys. Chem. Soc. 1903, 35, 211 ; Milobendzi and Sachnowski, Chem. Soc. Abst. 1918, i. 477) ; from C_2H_5I and $Pb_3(PO_3)_2$ (Michaelis and Becker, Ber. 1897, 1005). Colourless mobile liquid with an alliaceous odour.

3. *Ethyl-phosphorous acid* $H_2(C_2H_5)PO_3$, very unstable syrupy liquid ; obtained by action of PCl_3 upon weak alcohol (Wurtz, Ann. Chim. Phys. [3] 16, 218). The salts do not crystallise well, but are more stable than the acid.

Chloride of ethyl-phosphorous acid $C_2H_5POCl_2$; b.p 117·5° (corr.) ; sp.gr. 1·30526 at 0°/4° (Thorpe, Chem. Soc. Trans. 37, 346) ; from PCl_3

and C_2H_5OH (Menschutkin, Annalen, 139, 343) ; decomposed by water into HCl, C_2H_5OH, and H_3PO_3 ; also by heating to 165° into C_2H_5Cl, P, PCl_3, and P_2O_5 (Chambon, J. 1876, 205).

Diethyl pyro-phosphorous acid is not known, but the zinc salt $(C_2H_5)_2P_2O_5Zn$ is produced when $Zn(C_2H_5)_2$ is heated with P_2O_5 to 140° (Dilling, Zeitsch. Chem. 1876, 266).

Ethyl selenic acid $C_2H_5HSeO_4$, very unstable ; produced from H_2SeO_4 and C_2H_5OH (Fabian, Annalen, Suppl. 1, 244). The salts are also unstable, the most permanent being the strontium salt ; they can be crystallised with the ethyl-sulphuric acid salts.

Ethyl selenhydrate, *Ethyl selenomercaptan* C_2H_5SeH ; b.p. 53·5° ; sp.gr. 24°/4° 1·3954 (Tschugaeff, Ber. 1909, 42, 49). From ethyl iodide and sodium hydroselenide. Nauseous-smelling liquid.

Ethyl selenide, *Selenethyl* $(C_2H_5)_2Se$; b.p. 108° ; discovered by Löwig (Pogg. Ann. 37, 552). By action of K_2Se upon $(C_2H_5)_2C_2O_4$ (L.) ; by action of $KC_2H_5SO_4$ upon K_2Se (Joy, Annalen, 86, 35 ; Rathke, *ibid.* 152, 210) ; the crude product is then distilled again with KOH, $C_2H_5HSO_4$, and a small piece of P or S (Pieverling, *ibid.* 185, 331 ; Ber. 9, 1469). A colourless mobile liquid with a not unpleasant smell, is insoluble in water, acts as a base ; HCl precipitates from a solution in dilute HNO_3 an oily liquid $(C_2H_5)_2SeCl_2$, which gives with aqueous NH_3 a crystalline oxychloride $[(C_2H_5)_2Se]_2OCl_2$. Combines with C_2H_5I to form crystalline $(C_2H_5)_3SeI$ (Peverling). This is a white substance resembling Epsom salts in appearance. The $(C_2H_5)_2SeCl_2$ forms double salts with several metallic chlorides ; *e.g.* :

$$[(C_2H_5)_3SeCl]_2ZnCl_2$$

Ethyl diselenide $(C_2H_5)_2Se_2$; b.p. 186° ; formed as a by-product in the preparation of $(C_2H_5)_2Se$; was first obtained by Wöhler and Dean (Annalen, 97, 1) from $KC_2H_5SO_4$ and K_2Se_2 (Rathke, *ibid.* 152, 212) ; has an intensely disagreeable smell, and acts as a poison (Pieverling). A solution in dilute HNO_3 gives with HCl monoclinic crystals of $(C_2H_5)_2Se_2O_4(OH)_2Cl_2$, which are soluble in water, and are reduced by SO_2 to ethyl diselenide.

Ethoxy-selenyl chloride $C_2H_5O·SeOCl$; m.p. 10° ; b.p. 175°, not without decomposition. From $SeOCl_2$ and absolute alcohol. Heated in a tube to 200° yields Se, C_2H_5Cl, HCl, and H_2O (Michaelis and Landmann, Annalen, 241, 156).

Diethylselenite $SeO(OEt)_2$; b.p. 183°-185°, not without decomposition ; sp.gr. 1·49 at 16·5°. From $SeOCl_2$ and NaOEt in dry ether at 180°-190° ; also from Ag_2SeO_3 and C_2H_5I at 85° in sealed tube. A thick liquid, decomposed by water into C_2H_5OH and H_2SeO_3. Decomposed by heating in a tube at 200° with separation of Se (M. and L.).

Ammonium monoethylselenite

$$C_2H_5O·SeO·ONH_4 ;$$
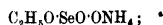
a crystalline, very hygroscopic acid, formed by action of alcohol and ammonia upon SeO_2 at temperature of melting ice. It is soluble in alcohol, insoluble in ether (Divers and Hada, Chem. Soc. Trans. 75, 538).

Ethyl sulphates.

Mono-ethyl sulphate $C_2H_5HSO_4$ *(Ethylsulphuric acid; Sulphethylic acid; Sulphovinic acid)*; sp.gr. 1·316 at 16°.

First noticed by Dabit (Crell's Ann. [1802] 1, 394); and again by Sertürner (Gilb. Ann. 60, 53; 64, 67, [1818-1820]; *see* also Hoeren, Pogg. Ann. 7, 193; Hennel, Trans. Roy. Soc. 1826; 240, 1828, 365; Serullas, Ann. Chim. Phys. [2] 39, 153; Liebig and Wöhler, Pogg. Ann. 22, 487; Liebig, Annalen, 9, 17, 32; 13, 32, 38; Dumas and Boullay, Ann. Chim. Phys. [2] 36, 300).

Formed by action of sulphuric acid upon alcohol (Dabit, Sertürner, Serullas); also by absorption of ethylene in sulphuric acid (Hennel; Berthelot, Ann. Chim. Phys. [3] 43, 385); by heating ether with strong H_2SO_4 (Hennel; Magnus, Pogg. Ann. 27, 386); from S_2Cl_2 and alcohol (Heusser, Annalen, 151, 249); from $HO\cdot SO_2Cl$ and alcohol in the cold (on heating, this gives $C_2H_5O\cdot SO_2Cl$, Claesson, J. pr. Chem. [2] 19, 245).

Preparation —A mixture of equal parts of absolute alcohol and strong sulphuric acid is heated for 4 hours on the water-bath; by this treatment 59 p.c. of the H_2SO_4 used is converted into mono-ethyl sulphate (Berthelot, Bull. Soc. chim. ii. 19, 295) By using 3 molecules alcohol and 1 molecule H_2SO_4 (*i.e.*, 3 to 2 by weight), 77 p.c. of the sulphuric acid is utilised (Claesson, J. pr. Chem. [2] 19, 246). The mixture is diluted with water and neutralised with lead or barium carbonate, filtered, evaporated to crystallisation, the crystals dissolved in water, and the acid set free by means of H_2SO_4, or, when lead carbonate is used, by means of H_2S. The excess precipitated $BaSO_4$, $PbSO_4$, or PbS is removed by filtration, and the liquid evaporated *in vacuó* over sulphuric acid. Mono-ethyl sulphate is a syrupy liquid, very soluble in water, soluble also in alcohol, but insoluble in ether.

Heated with water, yields alcohol and sulphuric acid; on heating with alcohol to 140°, ether and H_2SO_4 are formed. Oxidising agents, *e.g.* MnO_2 or K_2CrO_4, give aldehyde (Jacquemin and Lies-Bodard, J. 1857, 345) The salts are very soluble in water, and can be heated in dilute solutions without decomposition, though in strong solution, or by prolonged heating, they are decomposed with formation of alcohol, a sulphate, and free H_2SO_4. This decomposition may be diminished by the addition of an alkali hydroxide or carbonate. By dry distillation, the salts yield 'heavy oil of wine,' a liquid containing diethyl sulphate and olefines (*cf.* Kremann, Monatsh. 1917, 38, 53). HCl gas yields C_2H_5Cl and a metallic sulphate (Köhler, Ber. 19, 11, 1929).

By distilling sodium ethyl sulphate in a vacuum, Lilienfeld (Austrian Pat. 63526) obtains ethyl sulphate in 83–90 p.c. yield.

Salts (*v.* Marchand, Pogg. Ann. 32, 456; 41, 595). $LiC_2H_5SO_4,H_2O$; $NaC_2H_5SO_4,H_2O$; $KC_2H_5SO_4$, crystallises in anhydrous monoclinic plates, soluble in 0·8 part H_2O at 17°; (Schabus, J. 1854, 560; Marignac, J. 1855, 608).

$Mg(C_2H_5SO_4)_2,4H_2O$; $Ca(C_2H_5SO_4)_2,2H_2O$ forms monoclinic laminæ, soluble in 0·8 part water at 17° (M.); $Ba(C_2H_5SO_4)_2,2H_2O$, monoclinic plates, sp.gr. 2·080 at 21·7°, soluble in 0·92

parts of water at 17° (M.); $Pb(C_2H_5SO_4)_2,PbO$, large rhombic tables — $Pb(C_2H_5SO_4)_2,PbO$, amorphous; soluble in 0·54 part H_2O at 17°.

Diethyl sulphate $(C_2H_5)_2SO_4$; sp.gr. 1·1837 at 19° (Claesson, J. pr. Chem. [2] 19, 257); b.p. 208° (with decomposition), 113·5° at 31 mm., 118° at 40 mm., 120·5° at 45 mm. (Villiers, Bull. Soc. chim. ii. 34, 26); m.p. about −24·5° (V.); occurs in 'heavy oil of wine.' Formed by leading SO_3 vapour into absolute ether (Wetherill, Annalen, 66, 117); in small quantity by distillation of $C_2H_5HSO_4$; by dropping alcohol into chloride of ethyl sulphuric acid $C_2H_5O\cdot SO_2Cl$, or by action of H_2SO_4 upon alcohol (Claesson); from Ag_2SO_4 and C_2H_5I (Stempnewsky, Ber. 11, 514). A mixture of 1 vol. absolute alcohol and 2 vols. H_2SO_4 is distilled slowly *in vacuó* (Villiers). Absolute alcohol is mixed with Nordhausen sulphuric acid, the ether separated by means of $CHCl_3$, and the product distilled *in vacuó* (Claesson and Lundvall, Ber. 13, 1699).

Is an oily liquid, with an odour like that of peppermint: insoluble in water, and slowly decomposed by that liquid even in the cold; when heated with water, yields alcohol, H_2SO_4 and $C_2H_5HSO_4$. Heated with alcohol, forms ether and $C_2H_5HSO_4$; warm baryta water forms alcohol and $Ba(C_2H_5SO_4)_2$ (Villiers).

Unsaturated hydrocarbons are present to the extent of about 5 p.c. in 'heavy oil of wine.'

Chloride of ethyl sulphuric acid $C_2H_5O\cdot SO_2Cl$; b p 151°–154° (corr) (Claesson, J. pr. Chem. [2] 19, 248), with slight decomposition; 93°–95° at 100 mm. (Muller, Ber. 6, 227). From C_2H_5Cl and SO_3, together with isomerides (*v. Ethyl chloride*); by dropping alcohol into SO_2Cl_2 (not *vice versá*; diethyl sulphate is then formed) (Behrend, J. pr. Chem. [2] 15, 28); from a salt of ethyl sulphuric acid and PCl_5 (Purgold, Ber. 6, 505); from ethyl chloroformate $ClCO_2C_2H_5$ and fuming sulphuric acid (Wilm, Ber. 6, 505); by passing C_2H_4 into HSO_3Cl, $SO_4H\cdot C_2H_4\cdot SO_2Cl$ is also produced (Müller, *ibid.* 6, 227).

A liquid with an irritating smell, exciting tears, and decomposed by contact with water into HCl, H_2SO_4 and alcohol. When the chloride is added to methyl alcohol or ethyl alcohol, ethyl sulphuric acid and CH_3Cl or C_2H_5Cl are produced; with amyl alcohol, amyl sulphuric acid and ethyl chloride are formed (Müller). If, on the other hand, absolute alcohol is dropped into the chloride, diethyl sulphate is produced (Claesson).

Bromethyl sulphuric acid

$CH_2Br\cdot CH_2\cdot OSO_2OH(?)$;
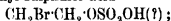
from ethylene bromide and SO_3 (Wroblewski, Zeitsch. Chem. 1868, 563). The barium salt is anhydrous, and is decomposed by continued heating with water, with separation of $BaSO_4$ and formation of glycol (Beilstein and Wiegand, Ber. 15, 1370). An isomeric body

$CH_3\cdot CHBr\cdot OSO_2\cdot OH(?)$
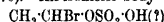
is formed by acting upon ethylene bromide with Ag_2SO_4 and water (B. and W.); the barium salt is very soluble in water, and its solution decomposes on warming into $BaSO_4$, HBr, and glycol.

Dibromo-diethyl sulphate $(CH_2Br\cdot CH_2)_2SO_4$; by action of ethylene bromide upon Ag_2SO_4 in

presence of benzene (Beilstein and Wiegand, Annalen, 15, 1369); a heavy oil insoluble in water, soluble in benzene and ether, decomposed on heating. Heated with water, yields bromide of ethyl sulphuric acid, and finally HBr, H_2SO_4, and glycol.

Ethyl sulphites.

Mono-ethyl sulphite $C_2H_5O \cdot SO \cdot OH$, *Ethyl sulphurous acid, Hyposulphethylic acid.* The potassium salt $KC_2H_5SO_3$ is obtained by passing SO_2 into a well-cooled solution of $NaOC_2H_5$ in absolute alcohol (Rosenheim and Liebknecht, Ber. 1898, 408). The ammonium salt is prepared by passing NH_3 followed by SO_2 into absolute alcohol (Divers and Ogawa, Chem. Soc. Trans. 1899, 535). The alkali salts are very unstable in the solid state decomposing with evolution of SO_2. Dilute mineral acids bring about this change in solution; ethyl iodide and alcohol at 150° yield ethyl sulphonate (*q.v.*). By treatment with PCl_5, diethyl sulphite yields the *chloride of ethyl sulphurous acid* $C_2H_5O \cdot SOCl$ which boils at 122°, is decomposed by water into HCl, SO_2, and alcohol, and gives, by further action of PCl_5 at 180°, thionyl chloride, C_2H_5Cl, and $POCl_3$ (Michaelis and Wagner, Ber. 7, 1074). Ethyl sulphurous acid is isomeric with ethyl sulphonic acid $C_2H_5 \cdot SO_2 \cdot OH$ (*q.v.*).

Diethyl sulphite $C_2H_5O \cdot SO \cdot OC_2H_5$; sp.gr. 1·1063 at 0° (Carius, J. pr. Chem. [2] 2, 279); b.p. 161·3°. From alcohol and S_2Cl_2; 18 parts of absolute alcohol are mixed with 50 parts of S_2Cl_2, previously warmed to 60°; the mixture is kept at this temperature for an hour, and then distilled: the portion boiling above 150° is redistilled (Warltz, Annalen, 143, 74).

A colourless liquid, with mint-like odour, miscible with alcohol and ether; insoluble in water. Decomposed by water; with PCl_5, yields a chloride C_2H_5OSOCl, which, on distillation, splits up into C_2H_5Cl and SO_2 (Geuther, Annalen, 224, 223; Michaelis and Wagner, Ber. 7, 1074). Decomposed by KOH into potassium ethyl sulphonate (Rosenheim and Liebknecht, *ibid.* 31, 405). Decomposes at 200° into SO_2 and ether (Prinz, Annalen, 223, 374); or by heating with $SOCl_2$, to 120°, into SO_2 and C_2H_5Cl (Geuther).

Ethyl sulphydrate C_2H_5SH. *Mercaptan, Ethyl mercaptan*; b.p. 36·2° (Nasini, Ber. 15, 2882); sp.gr. 0·83907 at 20°/4° (N.), 0·835 at 21°. By distilling $Ba(C_2H_5SO_4)_2$ with $Ba(HS)_2$ (Zeise, Annalen, 11, 1); by action of KHS upon C_2H_5Cl (Regnault, Ann. Chim. Phys. [2] 71, 390); by heating absolute alcohol saturated with SO_2 in a sealed tube, there are also formed $C_2H_5HSO_4$, $(C_2H_5)_2O$, and H_2SO_4 (Endemann, Annalen, 140, 336); from P_2S_5 and alcohol (Kekulé, Annalen, 90, 310). It is best prepared by saturating a solution of KOH, sp.gr. 1·3, with H_2S, mixing with a solution of $Ca(C_2H_5SO_4)_2$ (also of sp.gr. 1·3), and distilling on water-bath (Liebig, Annalen, 11, 14); according to Claesson (J. pr. Chem. [2] 15, 193), $(C_2H_5)_2S$ is also formed; NaC_2H_5S is prepared from the product of this action, the alcoholic solution evaporated to dryness, the $(C_2H_5)_2S$ removed by means of benzene, and the C_2H_5NaS decomposed by dilute H_2SO_4.

It is a colourless liquid with a penetrating garlic-like smell, slightly soluble in water, from which it crystallises on evaporation with $18H_2O$,

m.p. 12° (Claesson). It gives with bromine C_2H_5Br, HBr, and BrS (Friedel, Ladenburg, Annalen, 145, 189). HNO_3 forms $C_2H_5SO_3 \cdot 8C_2H_5$, or, if the acid is stronger, ethyl sulphonic acid. Treated with Cu powder, loses its disagreeable odour, but is considerably decomposed thereby (Finckh).

It forms crystalline compounds with $SiCl_4$ (Demarcay, Bull. Soc. chim. [2] 20, 127). It absorbs NO, forming a dark-red solution.

The hydrogen of mercaptan is replaceable by metals forming mercaptides; *e.g.* C_2H_5KS and $Hg(C_2H_5S)_2$, transparent plates, m.p. 76°-77° (Otto, Ber. 13, 1290; 15, 125), very slightly soluble in cold alcohol, soluble in 12-15 parts hot alcohol (Liebig, Annalen, 11, 17); gives with HNO_3 the nitrate $Hg(C_2H_5S)NO_3$ (Hofmann and Rabe, Zeitsch. anorg. Chem. 17, 26); $Pb(C_2H_5S)_2$, yellow precipitate, formed when $Pb(C_2H_5O_2)_2$ and C_2H_6HS are mixed in alcoholic solutions. $As(C_2H_4S)_3$, a foul-smelling oil formed from $AsCl_3$ and C_2H_5NaS, decomposed by heat into As and $(C_2H_5)_2S_2$. $Pt(C_2H_5S)_2$ pale-yellow precipitate (Zeise).

Ethyl sulphide $(C_2H_5)_2S$; b.p. 91° (Pierre, J. 1851, 51), 91·9° at 754·7 mm. (Beckmann, J. pr. Chem. [2] 17, 451), 92·2°–93° (corr.) at 754 mm. (Nasini, Ber 15, 2282); 92·1° (corr.) (Thorpe and Rodger); sp.gr. 0·8367 at 0° (Pierre), 0·83676 at 20°/4° (N.). From K_2S and C_2H_5Cl (Regnault, Ann. Chim. Phys. [2] 71, 387); from $Zn(C_2H_5)_2$ and $SOCl_2$ (Gauhe, Annalen, 143, 266); from KHS and $KC_2H_5SO_4$ in alcohol (Hobson, Chem. Soc. Trans. 10, 56); also from P_2S_5 and $(C_2H_5)_2O$ (Beckmann). To prepare the pure sulphide, heat the crude sulphide with Cu powder to 260°-280° (Finckh, Ber. 1894, 1239).

It is a colourless liquid with strong garlic-like smell, insoluble in water. Brühl states that in the pure state it has an ethereal odour. Chlorine acts upon it in the dark, forming substitution products: (1) $(C_2H_4Cl_2)_2S$, yellow liquid, b.p. 167°-172°, sp.gr. 1·547 at 12°; (2) $(C_2H_3Cl_3)_2S$, b.p. 189°-192°, sp.gr. 1·219 at 13·5°; (3) $(C_2HCl_4)_2S$, b.p. 217°-222°. By prolonged action of chlorine, C_2Cl_6 is formed, and possibly $(C_2Cl_5)_2S$ (Riche, Ann. Chim. Phys. [3] 43, 283; Annalen, 92, 358). $(C_2H_4Cl_3)_2S$ also results from action of chlorine upon $(C_2H_5Cl_2)_2S$, which can be obtained from C_2H_4 and Cl_2S_2 (Guthrie, Annalen, 116, 241). Bromine forms $(C_2H_4)_2SBr_2$, a yellowish-red unstable body, which, by the action of KI, yields $(C_2H_5)_2SI_2$, a black liquid (Rathke, Annalen, 152, 214).

Ethyl sulphide combines with many metallic chlorides to form crystalline compounds, *e.g.* $(C_2H_5)_2S \cdot HgCl_2$, white crystals, soluble in alcohol and ether, m.p. 119°; $(C_2H_5)_2S \cdot HgI_2$, yellow needles, m.p. 110°; $2(C_2H_5)_2S \cdot TiCl_3$, dark-red crystals (Demarcay). (For addition compounds, *see* Abel, Zeitsch. physiol. Chem. 20, 268; Werner, Zeitsch. anorg. Chem. 15, 14; 17, 101; Smiles, Chem. Soc. Trans. 1900, 164.)

Nitric acid (of sp.gr. 1·2) forms *ethyl sulphoxide* or *diethyl sulphine oxide* $(C_2H_5)_2SO$, a soluble oily liquid, solid at low temperatures, and decomposed by heating. Fuming nitric acid converts this into *diethyl sulphone* $(C_2H_5)_2SO_2$; b.p. 248°; m.p. 70°-72° (Oefele, Annalen, 127, 370; 132, 88); $R \cdot a = 47·53$ (Kanonnikow, J. Russ. Phys. Chem. Soc. 15

451); also formed from $Pb(C_2H_5)_4$ and SO_3 (Frankland and Lawrence, Chem. Soc. Trans. 35, 244), and from $(C_2H_5)_2S$, and a solution of $KMnO_4$ (O.). Rhombic plates, soluble in 6·4 parts water at 16°.

Triethyl sulphine $(C_2H_5)_3S$ forms compounds in which it plays the part of a univalent radical.

$(C_2H_5)_3SI$ from $(C_2H_5)_2S$, C_2H_5I, and H_2O (Oefele, Annalen, 132, 82); from HI and $(C_2H_5)_2S$ or HI and C_2H_5HS, or C_2H_5I and C_2H_4HS (Cahours, *ibid.* 135, 352; 136, 151); forms rhombic plates of disagreeable odour, and soluble in water. By action of Ag_2O, yields *triethyl sulphine hydroxide* $(C_2H_5)_3SOH$, a strong base; displaces NH_4, and has caustic action on the skin; it forms a crystalline deliquescent mass, which unites with acids to form deliquescent salts yielding double compounds with many metallic salts; *e.g.* :

$$PtCl_4 \cdot 2(C_2H_5)_3SCl$$
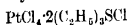
dark-reddish prisms, soluble at 20·7° in 30 parts of water (Dehn, Annalen, Suppl. 4, 90; Jorgenson, J. pr. Chem. [2] 6, 82; Kraut, Annalen, 210, 321).

When $(C_2H_5)_2S$ is heated with CH_3I, *diethylmethyl sulphine iodide* $(C_2H_5)_2CH_3SI$, an unstable non crystalline body, is formed, from which other salts can be obtained; the chloride $(C_2H_5)_3SCl$ forms many double salts (Kruger, J. pr. Chem. [2] 14, 196). The isomeride, *ethyl-methylethyl sulphine iodide,* prepared from $C_2H_5CH_3S$ and C_2H_5I, is crystalline (Kruger).

Ethyl disulphide $(C_2H_5)_2S_2$; b.p. 152·8°-153·4° (corr.) at 730 mm. (Nasini, Ber. 15, 2882); sp.gr. 0·99267 at 20°/4° (N.). By distillation of $KC_2H_5SO_4$ with K_2S_2 and water (Zeise, Annalen, 11, 1; Morin, *ibid.* 32, 267; Löwig, Kopp, *ibid.* 35, 345; Cahours, *ibid.* 61, 98); by action of 1 upon a slight excess of a solution of C_2H_5NaS (Kekulé; Linnemann, *ibid.* 123, 279); by action of S upon C_2H_5SNa (Böttger, *ibid.* 223, 348); by distilling liquid thioacetaldehyde (Klinger, Ber. 32, 2195).

A colourless liquid, with garlic-like smell, very slightly soluble in water; with dilute HNO_3, gives $(C_2H_5)_2S_4O_6$, an oily liquid, which may be regarded as the ethyl salt of ethyl thiosulphonic acid $C_2H_5SO_2SC_2H_5$.

Ethyl trisulphide $(C_2H_5)_2S_3$, from K_2S_3 and $KC_2H_5SO_4$ (Cahours, Bull. Soc. chim. [2] 25, 184); also from $(C_2H_5)_2S_2$ and S (H. Müller); a colourless liquid, with unpleasant smell.

Ethyl tetrasulphide $(C_2H_5)_2S_4$; from S_2Cl_2 and C_2H_5SH (Claesson, J. pr. Chem. [2] 15, 214); a heavy oily liquid, with disagreeable smell.

Ethyl pentasulphide $(C_2H_5)_2S_5$; by heating $(C_2H_5)_2S_4$ and S at 150°; a tough elastic solid.

Ethyl sulphinic acid $C_2H_5HSO_2$; by action of $Zn(C_2H_5)_2$ upon SO_2 (Wischin, Annalen, 139, 364; Hobson, Chem. Soc. Trans. 1858, 10, 58); the sodium salt is produced by oxidation of sodium mercaptide by dry oxygen (Claesson, J. pr. Chem. [2] 15, 199). The free acid is a syrupy liquid with a sweet taste; by action of HNO_3, yields ethyl sulphonic acid, and $(C_2H_5SO_2)_2NO$, crystals, m.p. 81·5°, very slightly soluble in water (Zuckschwerdt, Annalen, 174, 308). Forms salts, of which $NaC_2H_5SO_2$, crystallised from alcohol in anhydrous crystals (C.); the lead salt was prepared from $Pb(C_2H_5)_4$

and SO_2, by Frankland and Lawrence (Chem. Soc. Trans. 35, 244).

Ethyl chlorosulphinate $Cl \cdot SO_2 \cdot C_2H_5$. A faintly yellow liquid, b.p. 29°/13 mm., which decomposes at its b.p., 122°, under ordinary pressure, into sulphur dioxide and ethyl chloride, formed by treating well-cooled ethyl alcohol with thionyl chloride (Stähler and Schirm, Ber. 1911, 44, 319).

Ethyl sulphonic acid $C_2H_5 \cdot SO_2 \cdot OH$ by the oxidation of C_2H_5SH (Löwig and Weidmann, Pogg. Ann. 49, 329; Kopp, Annalen, 35, 346), C_2H_5CNS or of $(C_2H_5)_2S_2$ (Muspratt, Chem. Soc. Trans. 1849, 1, 45) by HNO_3; from C_2H_5I and K_2SO_3 (Graebe, Annalen, 146, 37). By heating ethylene sulphonic acid with P and HI at 170° (Kohler, Amer. Chem. J. 20, 688); by oxidation of C_2H_5CNS with hypochlorites (De Coninck, Compt. rend. 126, 838); by action of conc. HNO_3 upon mercury mercaptide nitrate (Hofmann and Rabe, Zeitsch. anorg. Chem 17, 26). The acid is a crystalline deliquescent body; by action of ICl_3 at 150°, we get *dichlorethyl sulphonic acid*; excess of ICl_3 gives C_2Cl_6 (Spring and Wessinger, Ber. 15, 445); unites with bases to form salts. (For halogen derivatives, *see* Kohler, Amer. Chem. J. 19, 737; 20, 690; 21, 361. For salts, *see* Rosenheim and Liebknecht, Ber. 31, 412.)

Ethyl sulphonate $C_2H_5 \cdot SO_2 \cdot OC_2H_5$; b.p. 213·4° (corr.); sp.gr. 1·1712 at 0°/0° 1·1452 at 20°/4° (Nasini, Ber. 15, 2884); by action of ethyl sulphonic chloride $C_2H_5SO_2Cl$ and C_2H_5NaO (Carius, J. 1870, 726; J. pr. Chem. [2] 2, 262); from C_2H_5I and silver sulphite or sodium ethyl sulphite (*q.v.*).

Ethyl sulphonic chloride $C_2H_5SO_2Cl$; b.p. 177·5° (corr.) (Carius), 171° (Otto, Ber. 15, 122); sp.gr. 1·357 at 22·5° (C.); by action of PCl_3 on $NaC_2H_5SO_3$ (Gerhardt and Chancel, Compt. rend. 35, 690); by action of Cl upon ethyl oxysulphide (S. and W. *l.c.*). Colourless liquid, with unpleasant smell.

Ethyl thiocyanate C_2H_5SCN; b.p. 143° (Berthelot, Compt. rend. 130, 444), 146° (corr.) (Buff, Ber. 1, 206); sp.gr. 1·033 at 0°, 1·0126 at 19°, 0·8698 at 146° (B.); by action of KCNS upon $KC_2H_5SO_4$ (Cahours, Ann. Chim. Phys. [3] 18, 264; Annalen, 6,1, 95), or C_2H_5Cl (Löwig, Pogg. Ann. 67, 101), or C_2H_5I (Johnson and Levy. Amer. Chem. J. 1907, 38, 456); from Et_2SO_4 and KCNS, yield 87 p.c. (Walden, Ber. 1907, 3214).

A mobile liquid with unpleasant odour, insoluble in water, miscible with alcohol or ether; by action of sodium forms NaCN and $(C_2H_5)_2S$ (Hofmann, Ber. 1, 184); by heating with solution of KOH, yields $(C_2H_5)_2S_3$, KCN, and KCNO (Brüning, Annalen, 104, 198); with alcoholic KOH, forms $(C_2H_5)_2S_3$, CO_2, NH_3, but no KCNS (Löwig), but with alcoholic KHS yields C_2H_5HS and KCNS (L.). Decomposed by hot solution of bleaching powder, yielding CO_2, N, $EtO \cdot SO_3 \cdot OH$, and H_2SO_4. NaClO and NaOH hot, yield $(EtO)_2SO_2$ and NaCN. Further action gives Et_2S_2, NaCN, and NaCNO, if all the hypochlorite is used up. By action of aqueous NH_3 at 100°, it yields $(C_2H_5)_2S_2$, NH_4CN, urea, oxalic acid, and other products (Kremer, J. 1858, 401; Jeanjean, J. 1862, 364). By passing Cl into it, there results (CNCl), and a liquid $C_2H_5SCl_4$, b.p. 134°-135° (James, J. pr.

Chem. [2] 30, 316). A chlorine substitution product C_2H_4ClSCN was obtained by James (*ibid.* [2] 20, 352) by heating C_6H_4ClBr with KCNS and alcohol; an oil heavier than water, with unpleasant smell; b.p. 202°-203°; m.p. below −20°.

Ethyl thiocyanate forms compounds with HCl, HBr, and HI (Henry, J. 1868, 652; Glutz, Annalen, 153, 312). (For many other compounds, *see* Wheeler and Johnson, Amer. Chem. J. 26, 345; J. Amer. Chem. Soc. 24, 680; Wheeler and Jamieson, *ibid.* 24, 743; Wheeler and Merriam, *ibid.* 24, 439.)

Ethyl *iso***thiocyanate** C_2H_5NCS (L.), *Ethyl-thiocarbimide, mustard oil*; b.p. 134°; sp.gr. 1·0192 at 0°, 0·9972 at 22°, 0·8763 at 133·2° (Buff, Ber. 1, 206); by action of C_2H_5NCO upon P_2S_5 (Michael and Palmer, Amer. Chem. J. 6, 259), also in very small quantity when $Hg(CNS)_2$ is heated with C_2H_5I (Michael, *ibid.* 1, 417), also by heating $CSCl_2$ and $(C_2H_5)NH_2$ (Rathke, Annalen, 167, 211). A solution of ethylamine in alcohol is treated with CS_2, when crystals of ethyl ammonium ethyl dithiocarbamate separate out, $2(C_2H_5)NH_2 + CS_2 = (C_2H_5)NH·CS·S·NH_3(C_2H_5)$. A solution of this body is then treated with $HgCl_2$, when the mercury compound is precipitated:

$(C_2H_5)NH·CS·S·NH_3(C_2H_5) + HgCl_2$
$= 2(C_2H_5)H_3NCl + [NH(C_2H_5)CS_2]_2Hg$
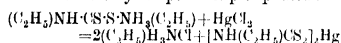
On distillation, this body yields the mustard oil, HgS and H_2S (Hofmann, Ber. 1, 171; 2, 452). Delépine (Compt. rend. 144, 1125) improves the yield of dithiocarbamate by using 1 molecule each of CS_2, amine, and soda, and then distilling with basic lead acetate in place of $HgCl_2$. Mustard oil is a liquid with very disagreeable smell, and in contact with the skin produces a burning sensation (Hofmann, Ber. 1, 26); with absolute alcohol forms monoethyl thiourethane $(C_2H_5)NH·CS·OC_2H_5$, a liquid, b.p 204°-208°; with aldehyde ammonia yields the compound $C_7H_{15}N_3S$, m.p. 135°·136° (Dixon, Chem. Soc. Trans. 1888, 414)

Thiocarbimides react with phenylhydrazine, yielding thiosemicarbazides (Marckwald) With Br in chloroform a ring compound, $C_4OS_2(NEt)_2$, melting at 45°, is formed (Freund and Bachrach, Annalen, 285, 184).

Ethyl thiophens $C_4SH_3(C_2H_5)$.

2-*Ethyl thiophen*; b.p. 132°-134° (corr.), sp.gr. 0·990 at 24°. By action of C_2H_5Br and Na upon C_4SH_3I (Meyer and Kreis, Ber. 17, 1560); also by action of Br upon thiophen, C_2H_5Br and Na (Schleicher, *ibid.* 18, 3015; *ibid.* 19, 671).

3-*Ethyl thiophen*; b.p. 135°-136°; sp¹gr. 1·0012 at 16°. By heating ethyl succinic acid with P_2S_3 (Damsky, Ber. 19, 3284; Gerlach, Annalen, 267, 146).

Di-ethylthiophen; b.p. 181°; sp.gr 0·962 at 14°/14°. An oil obtained by action of Na upon C_2H_5I and iodoethylthiophen (Muhlert, Ber. 19, 633).

Ethyl telluride $(C_2H_5)_2Te$, *Tellurethyl*; b p. 137°-138° (Marquardt and Michaelis, Ber. 21, 2045; Heeren, J. 1861, 565); from K_2Te and $KC_2H_5SO_4$ (Wöhler, Annalen, 84, 69; 35, 111; Mallet, Chem. Soc. Trans. 1853, 5, 71). A heavy, viscid, reddish-yellow liquid, with a very unpleasant smell, burns in air with blue flame, evolving fumes of TeO_2; hardly soluble

in water, and oxidised by exposure to air; is poisonous. HNO_3 forms $(C_2H_5)_2Te.2HNO_3$ (monoclinic prisms). Strong HCl precipitate, the oily compound $(C_2H_5)_2TeCl_2$ from a solution of the nitrate; ammonia converts this into $[(C_2H_5)_2Te]_2Cl_2O$ (hexagonal prisms), which, when treated with Ag_2SO_4, yields

$$[(C_2H_5)_2Te]_2,H_2SO_4$$
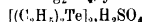
(colourless prisms). By action of Ag_2O upon a solution of the chloride, $(C_2H_5)_2TeO$ is produced, which decomposes on concentration.

When $(C_2H_5)_2Te$ is acted upon by C_2H_5I, *triethyl tellurium iodide* $(C_2H_5)_3TeI$ is formed, m.p. 90°-92° (Cahours, Bull. Soc. chim. [2] 4, 40), which crystallises in yellow prisms.

Ethyl ditelluride $(C_2H_5)_2Te_2$ is said to be formed in the preparation of $(C_2H_5)_2Te$, and to be a dark-red liquid, with high boiling-point.

ETHYLAMINES

Compounds in which one or more atoms of H in NH_3 are replaced by C_2H_5.

Ethylamine $C_2H_5·NH_2$; b.p. 18·7°, sp.gr. 0·6964 at 8°, 0·708 at 2° (Hofmann, Ber. 22, 699); m.p. −85·2°, b.p. 19° to 20° (Ladenburg and Krugel); sp.gr. 0·7013 at 4° 0·6892 at 15° (Perkin); crit. temp. 185·2° (Schmidt); 183·2° and crit. press. 55·4 atm. (Berthoud); H C.=408·5 Cals. (Berthelot, Ann. Chim. Phys. [5] 23, 244). From ethyl carbimide and KOH (Wurtz, Annalen, 71, 339; also Compt. rend. 28, 223); from C_2H_5Br and NH_3 (Hofmann, Annalen, 74, 159); by the putrefaction of yeast and of flour (Hesse, J 1857, 403; Sullivan, J. 1858, 231); by heating alcohol with NH_4Cl at 300° (Berthelot, Ann Chim Phys. [3] 38, 63); by action of nascent H upon acetonitrile(Mendius, Annalen, 121, 142). It is also produced in the dry distillation of the residues from beet-root in sugar manufacture (Duvillier and Buisine, Ann. Chim. Phys. [5] 23, 317); by action of $KC_2H_5SO_4$ upon alcoholic NH_3 at 120° (Erlenmeyer and Carl, J. 1875, 617); by action of Na upon $CH_3·CONH_2$ in boiling amyl alcohol (Guerbet, Compt rend 129, 62); from EtOH and phosphates at 225°-250° (Vidal, D. R. P. 64346); by action of Zn filings and HCl in the cold on aldehyde ammonia (Trillat and Fayollat) (Jean); by electrolytic reduction of nitroethane in H_2SO_4 at 70°-75° (Pieron, Bull. Soc. chim. [3], 21, 784)

Preparation.—(1) 1 volume of ethyl nitrate $C_2H_5NO_3$ is treated with 3 volumes of alcoholic ammonia for 12 hours at 100°; the free bases are separated from the NH_3 by neutralising with H_2SO_4 or HCl and extracting with alcohol; the sulphates or chlorides are then decomposed by NaOH, and the free bases combined with picric acid and crystallised. The picrate of $(C_2H_5)_3N$ separates first, in yellow needles, then the $C_2H_5NH_2$ salt in brown prisms; the picrates are then separated and decomposed by HCl, and the bases liberated by KOH (Carey Lea, Chem. News, 5, 118).

(2) Crude C_2H_5Cl, from manufacture of chloral, is heated for an hour with 3 times its volume of alcohol (95 p.c.) previously saturated with ammonia, in an iron vessel heated by a water-bath. On cooling, the NH_4Cl is filtered off, and the remainder distilled until free from NH_3 and alcohol, the residue (hydrochlorides of

mon-, di-, and tri-ethylamine, mixed with a little NH₄Cl) is treated with a strong solution of NaOH, and the liquid drawn off and dried by means of solid NaOH ; it consists of a mixture of the three bases ; ethyl oxalate is then added, and the $(C_2H_5)_3N$, which is unacted upon, is distilled off ; the residue consists of a mixture of solid *diethyl oxamide* $C_2O_2(NHC_2H_5)_2$ and liquid *ethyl diethyloxamate* $C_2O_2N(C_2H_5)_2OC_2H_5$, which are separated and the diethyl oxamide, after recrystallising from hot water, decomposed with KOH (Hofmann, Ber. 3, 109, 776 ; also Duvillier and Buisine, Compt. rend. 88, 31).

According to Garner and Tyrer (Chem. Soc. Trans. 1916, 109, 174), a mixture of mono-, di-, and tri-ethylamine can be separated by fractionating with a 10-bulb column.

(3) By the interaction of ethyl bromide and excess of ammonia in alcoholic solution. By regulating the addition of the ethyl bromide to the ammoniacal solution it is possible to obtain the primary and secondary bases without any sensible admixture of the tertiary base (*see* Werner, Chem. Soc. Trans. 1918, 113, 899).

Properties.—Is a mobile liquid, with strong ammoniacal odour, is strongly caustic, and has an alkaline reaction ; burns with yellow flame, is miscible in all proportions with water, displaces NH_3 from its salts, and, like ammonia, precipitates metallic hydroxides and oxides from salts. It, however, dissolves the hydroxides of Al (Wurtz), Au, and Ru (Carey Lea), and does not dissolve those of Cd, Ni, and Co. The chloride is decomposed on distillation into $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3, C_2H_4, and C_2H_5Cl (Fileti and Piccini, Ber. 12, 1508). CrO_3 oxidises ethylamine to aldehyde and N (Carstanjen, J. 1862, 330).

Caro's acid oxidises $EtNH_2$ yielding CH_3COOH, CH_3CN, $CH_3CH:NOH$, nitroethane, and $CH_3C(OH)NOH$ (Bamberger, Ber. 35, 4293). It forms a compound C_2H_5NHK (Titherley).

Salts (*v.* Wurtz, Annalen, 76, 329).— $(C_2H_5)NH_2,HCl$, deliquescent plates ; m.p. 76°–80° ; b.p. 315°–320° (with decomposition) ; sp.gr. 1·2045 at 21°/4° (Schiff and Monsacchi) ; molecular refract. 35·97 (calc. 35·95) (Kanonnikow, J. pr. Chem. [2] 31, 347) ; soluble in alcohol ; soluble in 0·42 part of water at 17° (S. and M. Zeitsch. physikal. Chem. 24, 513). Prepared by heating 1 volume of C_2H_5Cl with 3 volumes alcoholic ammonia to 100° (Groves, Chem. Soc. Trans. 1861, 13, 331). The hydrochloride and hydroiodide exhibit isodimorphism ; both are monoclinic at ordinary temperatures, changing at higher temperatures to uniaxial modifications. $C_2H_5NH_2,HgCl_2$, by action of alcoholic $HgCl_2$ on alcoholic $C_2H_5NH_2$; crystalline precipitate, soluble in hot HCl solution. With excess of $HgCl_2$ in aqueous solution a white precipitate

$$2C_2H_5NH_2,HgCl_2 + 2HgO$$
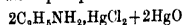
is thrown down ; by heating $C_2H_5NH_2$ with excess of $HgCl_2$, a yellow precipitate
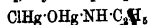
$$ClHg\cdot OHg\cdot NH\cdot C_2H_5$$

separates, whilst a crystallisable compound $ClHg\cdot NH\cdot C_2H_5$ remains in solution (Köhler, Ber.

12, 2308). $C_2H_5NH_2,PtCl_4$, yellow powder, combines with $(C_2H_5)NH_2$, and forms

$$4C_2H_5NH_2,PtCl_4,2H_2O$$
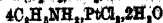
colourless crystals, soluble in water.

$(C_2H_5\cdot NH_2,HCl)_2,PtCl_4$, orange-yellow flat rhombohedrons (Weltzien, Annalen, 93, 272), hexagonal rhombohedrons (Topsoë, J. 1883, 619) ; sp.gr. 2·255 at 19°/4° (Clarke, Ber. 12, 1399). $C_2H_5NH_2,HCl,AuCl_3$, golden-yellow monoclinic prisms, soluble in water (T.).

$(C_2H_5NH_2)_2,H_2SO_4$, deliquescent body, soluble in alcohol ; forms double salts with other sulphates, *e.g.* ethyl-ammonium alum

$$(C_2H_5NH_2)_2,H_2SO_4,Al_2(SO_4)_3,24H_2O$$
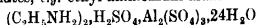
octahedral crystals, soluble at 25° in 6·89 parts of water.

Ethylchloramine C_2H_5NHCl. A very pungent-smelling oil ; sp.gr. 1·067 at 0° ; formed by action of NaClO upon $C_2H_5NH_2,HCl$. Heated with HCl, yields ethylamine (Berg, Ann. Chim. Phys. [7] 3, 319).

Ethyldichloramine, *ethylnitrogenchloride* $C_2H_5\cdot NCl_2$; b.p. 88°–89° at 762 •mm. ; sp.gr. 1·230 at 15° ; by passing Cl through aqueous $C_2H_5NH_2$ (Wurtz, Compt. rend. 11, 810), prepared by distilling a mixture of $C_2H_5NH_2,HCl$ with 2½ times its weight of bleaching powder and a little water (Tscherniak, Ber. 9, 146), a yellow oily liquid with a penetrating smell, insoluble in water and acids, decomposes on long standing into HCl, $NH_2Cl,C_2H_5NH_2,HCl$, $CHCl_3$, CH_3CN, and $CH_3\cdot COCl$ (Köhler, Ber. 12, 1870). The pure substance keeps unchanged for long periods under water (Tscherniak, *ibid.* 12, 2129). Alkalis decompose it into acetic acid and NH_3 ; behaves towards many bodies as free Cl. $Zn(C_2H_5)_2$ forms $(C_2H_5)_3N$ and $ZnCl_2$.

Ethyl di-iodoamine $C_2H_5NI_2$, and *Ethyl dibromamine* $C_2H_5NBr_2$, are formed similarly ; the former is a dark-blue liquid (Wurtz).

Ethyl nitramine $C_2H_5NH.NO_2$; m.p. +6° ; sp.gr. 1·1675 at 15°. A colourless liquid, with an acid reaction, prepared by the action of NH_3 upon diethyl dinitro-oxamide. It gives two classes of alkyl derivatives (Umbgrove and Franchimont, Rec. trav. chim. 16, 388). It is also formed from methyl ethylcarbamate and conc. HNO_3 (Franchimont and Klobbie, *ibid.* 7, 356).

Nitroethylisonitramine $CH_3\cdot CHNO_2\cdot N(OH)NO$ is obtained by the action of NO upon the Na derivative of nitroethane. It forms metallic salts, which are hydrolysed by mineral acids, giving NO and ethylnitrolic acid (Traube, Annalen, 300, 106).

Diethylamine $(C_2H_5)_2NH$; m.p. −40° (Hofmann, Ber. 22, 699) ; b.p. 57·5° (Hofmann, Annalen, 73, 91), 55·5° at 759 mm. (Oudemans, Rec. trav. chim. 1, 59) ; crit. temp. 223·3, crit. press. 36·6 atm. (Berthoud) ; sp.gr. 0·7262 at 0°, 0·7107 at 15° (Hofmann, Ber. 22, 669), 0·7226 at 4°, 0·7116 at 15°, 0·7028 at 25°. From NH_3 and C_2H_5I (Hofmann), or NH_3 and $C_2H_5NO_3$ (Lea, J. 1861, 493 ; *cf.* Garner and Tyrer, *l.c.*). From C_2H_5Br (Werner, Chem. Soc. Trans. 1918, 113, 899). Prepared by the action of KOH upon the $C_2O_2N(C_2H_5)_2OC_2H_5$ obtained in manufacture of ethylamine (*q.v.*).

Also by action of very dilute NaOH solution upon $[(C_2H_5)_2N(NO)]_2,H_2SO_4$ (Kopp, Ber. 8, 622). Also by action of EtOH upon phospham

at 225°–250° (Vidal, D. R. P. 64346). By heating p-toluenesulphodiethylamide with chlorsulphonic acid at 130°–150° (Marckwald and v. Droste-Hülshoff, Ber. 31, 3263). By dissolving 50 grams diethylaniline in 148 grams HCl (sp.gr. 1·1), diluting with 75 c.c. H₂O, adding 32 grams NaNO₂ in 50 c.c. H₂O and pouring slowly through a reflux condenser into a boiling solution of 85 grams NaOH in 2 litres of H₂O (Norris and Kimberley, Amer. Chem. J. 20, 60).

Price, Brazier, and Wood (J. Soc. Chem. Ind. 1916, 35, 147) have described a convenient mode of preparing large quantities of diethyl-amine in the laboratory by a simple modification of this method

$$NO \cdot C_6H_4 \cdot NEt_2 + NaOH$$
$$= NHEt_2 + NO \cdot C_6H_4 \cdot ONa$$
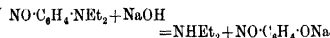
It a colourless, inflammable liquid with strong ammoniacal smell, very soluble in water; is a strong base, and acts like $C_2H_5NH_2$, except that it does not dissolve $Zn(OH)_2$ (Carey Lea). H_2O_2 oxidises it to diethylhydroxylamine (Dunstan and Golding). The nitrate decomposes suddenly at 170°, and yields nitrosodiethyl-amine $(C_2H_5)_2NNO$ (Franchimont, Rec. trav. chim. 2, 95); the hydrochloride $(C_2H_5)_2NH,HCl$ forms non-deliquescent plates; m.p. 215°–217° (Wallach, Annalen, 214, 275); b.p. 320°–330° (W.); sp.gr. 1·0475 at 21°/4° (Schiff and Monsacchi); and combines with many metallic chlorides, e.g. $[(C_2H_5)_2NH,HCl]_2PtCl_4$, orange-yellow monoclinic crystals (Topsoe, J. 1883, 619).

Diethylchloramine $(C_2H_5)_2NCl$. A pungent-smelling oil; b.p. 91°; sp.gr. 0·943 at 0°; formed by action of NaClO upon $(C_2H_5)_2NH$. It decomposes on keeping with formation of $(C_2H_5)_2NH,HCl$ (Berg, Ann. Chim. Phys. [7] 3, 320).

Diethylnitramine $Et_2N \cdot NO_2$; b.p. 206·5° at 757 mm., 93° at 16 mm.; sp.gr. 1·057 at 15°. Formed by action of EtI upon $EtNK \cdot NO_2$; also by action of highest concentrated HNO_3 upon as-diethylurea. It is decomposed by KOH at 150°–160° into $EtNH_2$, HNO_3, and CH_3CHO (Franchimont, Rec. trav. chim 6, 149; F. and Umbgrove, ibid. 16, 396).

Diethylisonitramine. An oil, b.p. 46°–50° at 18 mm.; sp.gr. 1·000 at 15°; formed by inter-action of EtI and $C_2H_5NAgNO_2$. KOH at 100° decomposes it into alcohol, N, and CH_3CHO (U. and F. l.c. 399).

Nitrosodiethylamine $(C_2H_5)_2NNO$; b.p. 176·9° (corr.); sp.gr. 0·951 at 17·5°; V D. = 3·36 (calc. = 3·53) (Knecht, Ber. 10, 979); by distilling neutral solution of $(C_2H_5)_2NH,HCl$ with a concentrated solution of KNO_2 (Geuther, Annalen, 128, 251; J. 1871, 695); also from $(C_2H_5)_2NH$ and NOCl in ether solution at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431); a yellow oil with aromatic smell, decomposed by HCl into $(C_2H_5)_2NH$ and HNO_2. Alcoholic KOH at 140° forms NH_3 and $(C_2H_5)NH_2$. Na amalgam forms N_2O and $(C_2H_5)_2NH$.

Triethylamine $(C_2H_5)_3N$; b.p. 89°–89·5° at 736·5 mm. (Bruhl, Annalen, 200, 186), 89°–90·5° at 767·8 mm. (Hofmann); sp.gr. 0·735 at 15° (Hofmann, Ber. 22, 700), 0·7426 at 4°, 0·7331 at 15°, 0·7527 at 25° (Perkin); crit. temp. 267·1° (Pawlowski, Ber. 16, 2633); remains liquid at −75° under 40 mm. pressure (H.). By the

action of NH_3 upon C_2H_5I (Hofmann, Annalen, 73, 91, or upon $C_2H_5NO_3$ (Carey Lea).

Preparation.—(1) Crude ethylamine (from C_2H_5Cl and NH_3) in alcoholic solution is treated with C_2H_5Cl (Duvillier and Buisine); (2) by distillation of $(C_2H_5)_4N \cdot OH$.

Properties.—An oily liquid with strong ammoniacal smell, slightly soluble in water; strong base. On strongly heating its salts, $(C_2H_5)_3N$ is destroyed, with formation of a little $(C_2H_5)_2N \cdot NO$ (Geuther, Zeitsch. Chem. 1886, 513).

The hydrochloride forms feathery non-deliquescent scales, and combines with many metallic salts to form double compounds. $N(C_2H_5)_3,HCl$, sp.gr. 1·06885 at 21°/4°. 1 part of water dissolves 1·5 parts salt (Schiff and Monsacchi). $(C_2H_5)_3N,HNO_3$, m.p. 98°–99° (Franchimont, Rec. trav. chim. 2, 339).

Tetra-ethylammonium hydroxide

$$(C_2H_5)_4N \cdot OH$$

formed from the iodide $(C_2H_5)_4NI$ by the action of Ag_2O. It forms very deliquescent needles, is a strong base, which eagerly absorbs CO_2, displaces NH_3, precipitates metallic hydroxides, and gives a blue solution with sugar and $CuSO_4$; is decomposed by dry distillation, forming triethylamine, ethylene, and H_2O; when heated with C_2H_5I, gives $(C_2H_5)_4I$ and alcohol.

Salts.—$(C_2H_5)_4NCl$, forms deliquescent crystals, sp.gr. 1·0801 at 21°/4° (Schiff and Monsacchi), and yields many double salts, e.g. $[(C_2H_5)_4NCl]_2HgCl_2$, tetragonal crystals; $(C_2H_5)_4NCl,HgCl_2$, triclinic crystals (Topsoe, J. 1883, 620); $[(C_2H_5)_4NCl]_2PtCl_4$, orange-yellow, crystalline (monoclinic (T)), difficultly soluble in water, almost insoluble in alcohol; $(C_2H_5)_4NBr$, light-orange needles, m.p. 78°, combines with Br to form an unstable pentabromide (Marquart, Ber. 3, 284); gives with alcoholic I solution a precipitate of $(C_2H_5)_4NI_3$, quadratic prisms (Weltzien, Annalen, 91, 33), which is also formed along with iodoform when the monoiodide is electrolysed between platinum electrodes (Goecke, Zeitsch. Elektrochem. 10, 249); the monoiodide $(C_2H_5)_4NI$ forms large crystals soluble in cold water and in alcohol, insoluble in ether; sp.gr. 1·559 (Schroder, Ber. 12, 562).

a-Ethyl hydroxylamine $C_2H_5O \cdot NH_2$; b.p. 68°; sp.gr. 0·8827 at 7·5° (Gurke, Annalen, 205, 277); by the action of HCl upon benzoyl ethylhydroxyl-amine ethyl ether $C_6H_5CO \cdot NC_2H_5 \cdot OC_2H_5$, or upon the ethyl ether of benzaldoxime

$$C_6H_5 \cdot CH : NOC_2H_5$$
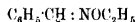
(Lossen and Zanni, ibid. 182, 223).

A strongly smelling inflammable liquid, miscible with water, alcohol, or ether; gives with $AgNO_3$ a white precipitate, which, on heating, is changed to metallic silver; with acids, forms salts, e.g. C_2H_5ON,HCl, scaly plates, m.p. 128°, decomposed by heating with HCl to 150° into C_2H_5Cl, NH_3O, HCl, and NH_4Cl; unites with $PtCl_4$ to form $(C_2H_5ON,HCl)_2PtCl_4$; prismatic crystals, soluble in water and in absolute alcohol (Lossen and Zanni). The sulphate $(C_2H_7ON)_2H_2SO_4$ crystallises with difficulty, and is soluble in water and in alcohol.

β-Ethyl hydroxylamine $C_2H_5NH \cdot OH$; m.p. 59°–60°, with decomposition; sp.gr. 0·9079 at 63·0° (Bruhl). Formed by heating for 8 hours at 140°, β-ethyl-a-benzylhydroxylamine

with conc. HCl (Behrend and Leuchs, Annalen, 257, 228); from hydroxylamine and EtI (Lobry de Bruyn, Rec. trav. chim. 13, 48; Hantzsch and Hilland, Ber. 31, 2065; Dunstan and Golding, Chem. Soc. Trans. 75, 807); by heating 1 part *m*-nitrobenzylaldoxime-N-ethyl ether with 7 parts conc. HCl (Kjellin, Ber. 26, 2378); by electrolytic reduction of nitroethane in H₂SO₄ solution at 15°-20° (Pierron, Bull. Soc. chim. [3] 21, 784).

It is very easily soluble in water or alcohol, less so in ether, benzene, or cold ligroin. It reduces Barreswil's solution, and is reduced by HI to C₂H₅NH₂.

ββ-Diethyl hydroxylamine (C₂H₅)₂N·OH ; b.p. 130°-134°. with decomposition (Dunstan and Golding, b.p. at 15 mm. 47°-49° (Lachman) ; sp.gr. 0·8771 at 15°/15° (D. and G.), 0·8784 (L.). An oil formed by action of EtI upon NH₄OH, and also from (C₂H₅)₂NH and H₂O₂ (D. and G. Chem. Soc. Trans. 75, 800). From addition product of diphenylnitrosamine and Zn(Et)₂ by decomposition with water, along with diphenylamine and Zn(OH)₂ (Lachman, Ber. 33, 1022).

Is a feeble base, soluble in water, alcohol, or ether. Reduces AgNO₃ and Hg Cl₂, and, on heating, CuSO₄. Reduced with HI, yields (C₂H₅)₂NH.

αβ-Diethyl hydroxylamine C₂H₅NH·O C₂H₅ ; b.p. 83° ; sp.gr. 0·829 at 0° ; formed by interaction of α-ethylhydroxylamine and EtBr. It is easily soluble in water, alcohol, or ether. Heated with conc. HCl at 200°, yields HN₂(C₂H₅) and C₂H₅Cl (Lossen, Annalen, 252, 230).

The hydrochloride C₄H₁₁NOHCl of an isomeric compound is obtained by action of Sn and HCl upon C₂H₅NO₃ (Lossen, *ibid.* Suppl. 6, 238). The salts are more soluble in water than those of hydroxylamine. The free base is a syrup, easily soluble in water, and has strong basic properties. The platinum salt is in the form of orange-yellow plates, soluble in warm alcohol and in water.

Triethyloxamine (C₂H₅)₃NO is a colourless crystalline mass obtained from ββ-diethylhydroxylamine and EtI. Also from NEt₃ and H₂O₂ (Dunstan and Golding ; Lachman).

It is very easily soluble in water, less so in CHCl₃ and insoluble in ether. Decomposes on heating. Reduces Barreswil's solution on heating. It gives a precipitate with CuSO₄ and AgNO₃. On reduction, yields triethylamine.

Triethyl methyl ammonium iodide

N(C₂H₅)₃CH₃I
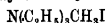
obtained by action of N(C₂H₅)₃ upon CH₃I (Hofmann, Annalen, 78, 277) (for other *Salts*, *v.* Topsoë, J. 1883, 620). The picrate melts at 267°-268° (Lossen, Annalen, 181, 374).

Diethyl dimethyl ammonium iodide, obtained from N(CH₃)₂H and C₂H₅I ; or from N(C₂H₅)₂H and CH₃I (V. Meyer and Lecco, Annalen, 180, 177) (for other *Salts*, *v.* Topsoë, *l.c.*). The picrate melts at 285°-287° (Lossen, Annalen, 181, 374).

Ethyl trimethyl ammonium iodide is formed from (CH₃)₃N and C₂H₅I (Müller, *ibid.* 108, 1) (for other *Salts, v.* Topsoë). The picrate melts at 299°-300° (Lossen).

Triethyl propyl ammonium iodide

N(C₂H₅)₃(C₃H₇)I
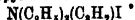
crystallises in large needles (Mendius, Annalen, 121, 136).

Diethyl *iso*amylamine N(C₂H₅)₂(C₅H₁₁) ; b.p. 154°; from the distillation of N(C₂H₅)₂(C₅H₁₁)OH (Hofmann) ; [N(C₂H₅)₂C₅H₁₁,HCl]₂PtCl₄, yellow needles.

Triethyl *iso*amyl ammonium iodide

N(C₂H₅)₃(C₅H₁₁)I
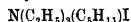
formed by the action of N(C₂H₅)₃ upon C₅H₁₁I (Hofmann, Chem. Soc. Trans. 1852, 4, 313 ; Annalen, 78, 279) ; the hydroxide decomposes on heating as follows :—

C₅H₁₁(C₂H₅)₃N·OH
    = N(C₅H₁₁)(C₂H₅)₂+C₂H₄+H₂O
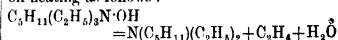
Diethyl methyl *iso*amyl ammonium iodide

N(C₂H₅)₂CH₃(C₅H₁₁)I
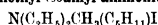
is formed from N(C₂H₅)₂(C₅H₁₁) and CH₃I (Hofmann).

Ethyl-methyl-*iso*amylamine

NC₂H₅(CH₃)(C₅H₁₁)
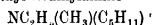
b.p. 135° ; is obtained by distillation of the hydroxide of the radical of the preceding compound (Hofmann).

Acetethylamide CH₃·CONHC₂H₅ ; b.p. 205°, sp.gr. 0·942 at 4·5° (Wurtz) ; b.p. 204°-205° (Titherley) ; from ethyl acetate and ethylamine (Wurtz, Ann. Chim. Phys. [3] 30, 491 ; Compt. rend. 36, 180 ; Annalen, 76, 334) or from C₂H₅NCO and HC₂H₃O₂ (Wurtz, *ibid.* 88, 315) ; from CH₃CONHNa and EtI at 150°. The hydrochloride forms deliquescent needles, melting at 60°. With NaNH₂ yields CH₃CONNaC₂H₅, which, with KMeSO₄, gives CH₃CONMeEt, an oil boiling at 180°, and soluble in water (Titherley, Chem. Soc. Trans. 1901, 393). By action of Cl yields *ethyl acetyl nitrogen chloride* NClEt(C₂H₃O) (Norton, Tcherniak, Bull. Soc. chim. [ii.] 30, 106 ; Compt. rend. 86, 1409), an oily unstable liquid, slightly soluble in water.

Acetdiethylamide N(C₂H₅)₂C₂H₃O ; b.p. 185°-186° ; sp.gr. 0·9248 at 8·5° (Wallach, Annalen, 214, 235).

Diacetylethylamide NC₂H₅(C₂H₃O)₂ ; b.p. 185°-192° (Wurtz) ; sp gr. 1·0092 at 20° (W.) ; by heating EtNCO with (C₂H₃O)₂O to 200° (Wurtz, Ann. Chim. Phys. [3] 42, 43).

Ethyl hydrazines ; Ethylamide.

1. *Ethyl hydrazine* C₂H₅HN·NH₂ ; b.p. 99·5° at 709 mm., is prepared by reducing nitrosodiethyl urea N(C₂H₅)H·CO·N(NO)C₂H₅ by means of zinc-dust and acetic acid ; this yields ethyl hydrazine urea (semi-carbazide) N(C₂H₅)H·CO·N(NH₂)C₂H₅, and this, by action of HCl, forms C₂H₅HN·NH₂, CO₂, and C₄H₅NH₂ ; by passing in HCl the chloride separates out, which is then decomposed by strong KOH solution and solid KOH, and the resulting oily liquid distilled over BaO (Fischer, Annalen, 199, 287) ; also by reducing ethylnitramine with Zn and HCl (Thiele and Meyer, Ber. 29, 963).

Is a colourless liquid, with faintly ammoniacal odour ; has great affinity for water, in which it is soluble, as also in alcohol, ether, chloroform, and benzene ; fumes in air and destroys cork and caoutchouc ; reduces Barreswil's solution in the cold. Br water liberates N. It precipitates metallic oxides, and gives the isonitrile reaction with KOH and CHCl₃. Forms two chlorides: (1) C₂H₆N₂,2HCl, white needles, very

soluble in water and alcohol ; on heating to 110°
yields (2) $C_2H_8N_2$,HCl, an amorphous horny
deliquescent body. The sulphate crystallises
from alcohol in thin plates, and is very soluble
in water. By heating $C_2H_8NH\cdot NH_2$ with $K_2S_2O_7$
at 80°–100°, potassium ethyl hydrazine sulpho-
nate $C_2H_5NH\cdot NHSO_3K$ is obtained ; this forms
fine needles, very soluble in water, much less
soluble in alcohol or ether (Fischer).

2. as-Diethylhydrazine $(C_2H_5)_2N\cdot NH_2$; b.p.
96°–99° ; prepared by action of zinc-dust and
acetic acid upon a solution of nitrosodiethyl-
amine $(C_2H_5)_2(NO)N$; 30 grams $(C_2H_5)_2(NO)N$
dissolved in 300 grams water are mixed with
150 grams Zn dust and 150 grams C_2H_4O (of
50 p.c.) kept at 20°–30°, and, towards the end, at
40°–50°. Excess of Zn is then dissolved by HCl,
an excess of NaOH added, and the mixture
distilled ; the distillate is neutralised with HCl
and NH_4Cl separated by crystallisation. From
the mother liquor $(C_2H_5)_2N_2H_2$ mixed with
$(C_2H_5)_2HN$ is freed by solid KOH. By the
action of HCNO diethylhydrazine urea (semi-
carbazide) $NH_2\cdot CO\cdot NH\cdot N(C_2H_5)_2$ is formed. 4
grams of this compound are heated with 15
grams of HCl in a sealed tube at 100°, diluted
and the NH_4Cl separated ; on treatment with
KOH, pure $(C_2H_5)_2N_2H_2$ is obtained (Fischer,
Annalen, 199, 308).

Is a colourless liquid with a faintly am-
moniacal smell, very hygroscopic and soluble
in water, alcohol, ether, chloroform, and ben-
zene ; reduces Barreswil's solution only on
warming ; is monobasic ; the salts are soluble in
water and alcohol, and difficult to crystallise.
$[(C_2H_5)_2N_2H_2\cdot HCl]PtCl_4$ forms fine yellow
needles, soluble in water. With $SOCl_2$ in ice-
cold ether, yields $(C_2H_5)_2N\cdot NSO$, an aromatic
oil, b.p. 73° at 20 mm. It is slowly hydrolysed
by water (Michaelis and Storbeck, Ber. 26,
310).

3. sym-Diethylhydrazine $C_2H_5\cdot HN\cdot NH\cdot C_2H_5$;
b.p. at 758 mm. 84°–86°. Formed by heating
at 100° for 3 hours 1 part sym-diethyl-diformyl-
hydrazide and 2 parts fuming HCl ; an oil ;
heated with conc. HCl, at 155°, yields NH_4Cl
and C_6H_5Cl. With yellow HgO forms $HgEt_2$.
With HNO_2 yields ethyl nitrite. The hydro-
chloride melts at 160° with decomposition
(Harries, Ber. 27, 2279).

Triethyl-azonium iodide $(C_2H_5)_3NNH_2I$ is
formed by action of diethylhydrazine upon 1½
times its weight of C_2H_5I (Fischer, Annalen,
199, 316). It forms needles very soluble in
water and in hot alcohol ; insoluble in ether and
strong alkalis. By action of Ag_2O, gives the
strongly alkaline free base, which, on heating,
yields $(C_2H_5)_2N\cdot NH_2$ and C_2H_4. By the action
of nascent H (Zn and H_2SO_4), the iodide yields
HI, NH_3, and $(C_2H_5)_3N$.

Tetra-ethyltetrazone $(C_2H_5)_2N\cdot N:N\cdot N(C_2H_5)_2$;
by the action of yellow HgO upon a cold aqueous
solution of $(C_2H_5)_2N\cdot NH_2$ (Fischer, Annalen, 199,
319) ; is an oily liquid with a disagreeable smell,
not volatile without decomposition, and which
does not freeze at −20°. When decomposed
by heat, yields N and $(C_2H_5)H_4N$. Forms an
explosive oily compound with I. Is a strong
base, though its salts are very unstable. It re-
duces silver solutions with formation of a mirror.
The solution decomposes on heating, yielding
N, $N(C_2H_5)_2H$, and aldehyde. The Pt double

salt $[(C_2H_5)_4N_4,2HCl]_2PtCl_4$ forms yellow prisms
soluble in water.

Ethylene C_2H_4, Olefiant gas, Heavy car-
buretted hydrogen, Bicarburetted hydrogen,
Elayl, Ethene, Etherin, discovered by Deiman,
Van Trootswyk, Bondt, and Lauwerenburgh
(Crell's Ann. 1795, [2] 195, 310, 430). Obtained
by action of H_2SO_4 upon alcohol ; the addition
of $Al_2(SO_4)_3$ increases the rate of production
(Senderens, Compt. rend. 1910, 151, 392).
The sulphuric acid can be replaced by syrupy
phosphoric acid, sp.gr. 1·75 (Newth, Chem. Soc.
Trans. 1901, 915) ; or alcohol vapour may be
passed over heated phosphoric acid, or over
thin layers of aluminium sulphate at 350°–400° ;
by the dry distillation of many organic bodies
(hence occurs to the extent of 4 or 5 p.c. in coal
gas). Also formed when CS_2 and H_2S (or PH_3)
are led over heated copper (Berthelot, Annalen,
108, 194). To prepare the gas, a mixture of
25 parts (by weight) of alcohol and 150 parts
sulphuric acid is heated to 170°, and a mixture
of 1 part of alcohol and 2 of H_2SO_4 is allowed to
drop slowly into the vessel by means of a funnel.
The gas is passed through H_2SO_4,NaOH solu-
tion, and then again through H_2SO_4. For the
preparation of small quantities of pure gas, an
alcoholic solution of $C_2H_4Br_2$ is warmed with
granulated Zn (Sabanejeff, J. Russ. Phys. Chem.
Soc. 9, 33). Equal volumes of CO and H led
over coke impregnated with reduced Ni and
Pd heated at 95°–100°, yield 8·3 p.c. C_2H_4
(Orloff, ibid. 40, 1588).

Ethylene is produced on an industrial scale
by the method of Maihle by passing the vapour
of alcohol over amorphous alumina heated to
360°. For details, see Spreut, J. Soc. Chem.
Ind. 1913, 171.

Properties.—A colourless gas, liquefied by a
pressure of 42½ atmospheres at −1·1° ; b.p.
−105° (Cailletet, Compt. rend. 94, 1224).
−102°–103° (Wroblewsky, Olszewsky, Monatsh.
4, 338), −103·9° (Burrell and Robertson) ;
m.p. −169°, b.p. at 757 mm. −104·3°, sp.gr.
0·6095 at −102·7° (Ladenburg and Krugel,
Ber. 32, 49, 1821) ; −102·5°, sp.gr. 0·565
(Maass and McIntosh, J. Amer. Chem. Soc.
1914, 36, 737) ; crit. temp. 9·5° ; becomes
liquid at 1° and 45 atmospheres, at 4° and 50
atmospheres, at 8° and 56 atmospheres, and at
10° and 60 atmospheres (C.) ; $L_D = 1\cdot26031$
(Batuecas, Helv. Chim. Acta, 1918, 1, 136).
1 volume of water absorbs at t°,

$$0\cdot25629 - 0\cdot009136t + 0\cdot0001881t^2$$

volumes C_2H_4 (Bunsen). Alcohol (of sp.gr. 0·792
at 20°) absorbs $3\cdot59498 - 0\cdot05772t + 0\cdot00681t^2$
volumes (Carius, Annalen, 94, 133) ; H.C.p.
$= 341\cdot4$ Cals. ; H.F. (from amorphous C) $= -9\cdot4$
Cals. (Berthelot, Ann. Chim. Phys. [5] 23, 180).

Ethylene forms an explosive mixture with
oxygen, and explodes, even in the cold, in con-
tact with ozonised oxygen (Houzeau and
Renard, J. 1873, 319). Led through a hot tube,
it splits up into C, H, CH_4, C_2H_6, and C_6H_6
(Berthelot, Annalen, 139, 277 ; Bone and
Coward, Chem. Soc. Trans. 1908, 1197). When
heated in an iron tube under a pressure of about
70 atmospheres it undergoes rapid polymerisa-
tion at 380°–400°. The liquid polymerisation
products consist of mixtures of saturated,
ethylenic, and polymethylene hydrocarbons ; viz.

iso-pentane, hexane, heptane, octane, nonane, amylene, hexylene, nonanaphthene, and $a\beta$ decyl, thene, hen-, deca-, dodeca-, tetradeca-, and pentadeca-naphthenes. At atmospheric pressure ethylene does not polymerise, even at 600° (Ipatieff, Ber. 1911, 44, 2978). Decomposed by leading over reduced Ni at 300° into C, C_2H_6, CH_4, and H (Sabatier and Senderens, Compt. rend. 124, 616, 1358). By the action of the electric spark it forms C_2H_2 and H, and then C and H (Wilde, Zeitsch. Chem. 1866, 735). It combines with H to form C_2H_6, when the mixture is passed through a hot tube (Ann. Chim. Phys. [4] 9, 431 ; Bull. Soc. chim. [ii.] 39, 145), or when in contact with Pt black in the cold (Wilde, Ber. 7, 354). By heating a mixture of C_2H_4 and CO_2 at 400°, aldehyde is formed (Schützenberger, Bull. Soc. chim. [ii.] 31, 482). CrO_3 converts it into aldehyde at 120° (Annalen, 150, 373). Fuming sulphuric acid absorbs readily large quantities of C_2H_4 at ordinary temperatures, as does also common H_2SO_4 at 160°-170° (Butlerow, Ber. 6, 193), forming $C_2H_5HSO_4$ (Faraday). C_2H_4 combines at 100° with strong HI or HBr solution, but not with HCl (Berthelot, Annalen, 104, 184 ; 115, 114). With bromine water forms a mixture of ethylene bromohydrin and ethylene dibromide (Read and Williams, Chem. Soc. Trans. 1917, 111, 240). N_2O_4 reacts with ethylene to form ethylene nitrosite, and N_2O_5 to form ethylene nitrate (Demjanow, Chem. Zentr. 1899, i. 1064). In presence of $AlBr_3$, HBr unites at 0° with C_2H_4, forming C_2H_5Br. With Cl_2O, *chlorethyl chloracetate* $CH_2Cl·CO·C_2H_4Cl$ is formed, whilst ClO_3 yields $CH_2Cl·CO_2H$. C_2H_4 combines with BF_3 in sunlight to form $C_2H_3BF_2$ (Landolph, B r. 12, 1586), a liquid, b.p. 124°-125°, sp.gr. 1·0478 at 23°. Ethylene acts as a divalent radical, and forms salts with most of the acids.

Ethylene acetates (Wurtz, Compt. rend. 43, 199 ; Atkinson, Phil. Mag. [4] 16, 433).

1. *Ethylene monoacetate* $C_2H_4(C_2H_3O_2)OH$, *monoacetic glycol* ; b.p. 190°-190·5° (corr.) (Perkin, Chem. Soc. Trans. 45, 505) ; sp.gr. 1·1108 at 15°/15°, 1·1018 at 25°/25° (P.) ; produced by action of $KC_2H_3O_2$ upon $C_2H_4Br_2$ in presence of alcohol (Atkinson, *l.c.* ; *cf.* Seelig, D. R. P. 41507). A liquid not miscible with water ; yields glycol $C_2H_4(OH)_2$ by heating with $C_2H_4Br_2$ and alcohol (Demole, Annalen, 177, 45) ; decomposed by heating with C_2H_3OCl into acetochlorhydrin and ethylene diacetate (Lourenço, *ibid.* 114, 127).

2. *Ethylene diacetate* $C_2H_4(C_2H_3O_2)_2$; b.p. 186°-187° ; sp.gr. 1·128 at 0° ; prepared from $C_2H_4Br_2$ or $C_2H_4I_2$ and $AgC_2H_3O_2$ (Wurtz, Ann. Chim. Phys. [3] 55, 433), or from $C_2H_4Br_2$ and anhydrous $KC_2H_3O_2$ at 150°-200° (Demole).

A liquid soluble in 7 parts of water, isomeric with *ethylidene diacetate* $CH_3·CH(C_2H_3O_2)_2$; b.p. 108·8° ; sp.gr. 1·061 at 12° ; prepared from aldehyde and $(C_2H_3O)_2O$. *Dichlorethylene diacetate* $C_2H_2Cl_2(C_2H_3O_2)_2$; b.p. 120° at 20 mm. ; is produced by action of chloracetic acid upon C_2H_2 (Prudhomme, Zeitsch. Chem. 1870, 397).

Ethylene acetochlorhydrin

$ClCH_2·CH_2·O·C_2H_3O$
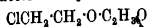
b.p. 145° ; sp.gr. 1·1783 at 0° ; by heating a mixture of glycol and acetic acid at 100° with HCl (Simpson, Annalen, 112, 147) ; from C_2H_4

and $CH_2Cl·CO_2H$ (Schützenberger and Lippman, *ibid.* 138, 325) ; insoluble in water ; yields ethylene oxide by action of KOH.

Ethylene acetoiodohydrin $ICH_2·CH_2·O·C_2H_3O$, heavy oil ; and

Ethylene acetobromohydrin

$BrCH_2·CH_2·O·C_2H_3O$
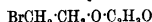
b.p. 161°-163° ; are prepared from

$C_2H_4(C_2H_3O_2)OH$
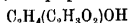
by action of HI and HBr respectively, the former in the cold in presence of $C_2H_4(OH)_2$ and $CH_3·CO_2H$ (Simpson, Annalen, 113, 123), the latter at 100° (Demole, *ibid.* 173, 120).

Ethylene glycols.

1. **Ethylene glycol** $CH_2OH·CH_2OH$; *glycol* ; m.p. −17·4° ; b.p. 197·37° (Ladenburg and Krugel, Ber. 32, 1821) ; b.p. 197°-197·5° at 764·5 mm. (Wurtz), 196°-199° (corr.) (Perkin, Chem. Soc. Trans. 45, 504), 195° at 751·3 mm. (Pribram and Handl, Monatsh. 2, 673) ; sp.gr. 1·125 at 0° (W.), 1·1279 at 0° (P. and H.), 1·1168 at 15°/15°, 1·112 at 25°/25° (Perkin).

Discovered by Wurtz (Compt. rend. 43, 199 ; Ann. Chim. Phys. [3] 55, 400). Formed by action of ethylene diacetate upon KOH (W.) ; from $C_2H_4Cl_2$ and moist silver oxide at 160°-200° (Simpson, Annalen, Suppl. 6, 253) ; by heating ethylene monoacetate with $Ba(OH)_2$ or with water in sealed tubes (Debus, Annalen, 110, 316) ; by heating a strong aqueous solution of neurine, when glycol and $N(CH_3)_3$ are formed (Wurtz, *ibid.* Suppl. 6, 200) ; by heating ethylene chloride or bromide with PbO and 15-20 times its volume of water at 140°-170° (Eltekow, Ber. 6, 558) ; or with ferric oxide, or with an alkali formate and an alcohol under pressure ; from ethylene bromide and water at 140°-150° (Niederist, Annalen, 186, 393) ; together with polyethylene glycol, by action of C_2H_4O (oxide of ethylene) upon water in sealed tubes (Wurtz, *ibid.* 113, 255).

A mixture of glycols, in which ethylene glycol predominates, may be prepared by decomposing petroleum vapours in an iron tube heated at about 650°, converting the product into dichlorethane, &c., purifying this compound by distillation and treating the distillates with alkali carbonates in a closed vessel (Hibbert, Met. & Chem. Eng. 1918, 19, 571).

Preparation.—1. 600 grams ethylene bromide, 700 grams fused potassium acetate, and 1500 grams alcohol (sp.gr. 0·83) are heated in a flask with reflux condenser until all action ceases ; cooled, filtered from KBr and filtrate distilled ; the portion distilled above 140° is decomposed by slight excess of $Ba(OH)_2$ and heated for 12 hours on water-bath. The excess of baryta is removed by CO_2, the liquid evaporated to one-third its volume, the residue treated with a mixture of alcohol and ether, the liquid removed from the crystals and distilled, first on water-bath, to separate alcohol and ether, then over the flame ; the portion distilling above 185° is then redistilled (Erlenmeyer, Annalen, 192, 244).

2. A mixture of 188 grams ethylene bromide, 138 grams potassium carbonate and 1 litre of water, [or 32 parts $C_2H_4Br_2$, 25 parts K_2CO_3, 350 parts H_2O (Groscheintz, Bull. Soc. chim. [ii.] 31, 203)], is heated with reflux condenser for

10 hours, is then evaporated to small volume on water-bath, the liquid portion poured off the crystals of KBr, the latter are washed with absolute alcohol. The filtrate and alcoholic washings are then distilled as in previous method; a loss owing to formation of C_2H_5Br is experienced by this process (Zeller and Hüffner, J. pr. Chem. [2] 11, 229). Haworth and Perkin (Chem. Soc. Trans. 1896, 175) obtained a 60 p.c. yield by digesting 138 grams K_2CO_3 in 1000 c.c. H_2O with 188 grams $C_2H_4Br_2$ under a reflux condenser. The solution is evaporated very slowly to a syrup, and then extracted with a mixture of alcohol and ether.

3. 1 part of ethylene bromide and 26 parts water are heated to 100° in a sealed vessel for 130 hours. This method gives a yield of over 60 p.c. of the theoretical amount (Niederist, Annalen, 196, 354).

4. Glycol diacetate is decomposed with powdered $Ca(OH)_2$, and the mixture distilled under reduced pressure. The yield of glycol is 93 p.c. of theory (Henry, Rec. trav. chim. 18, 221).

5. It may also be prepared by heating ethylene diacetate with methyl alcohol and hydrochloric acid (Henry, Bull. Acad. Roy. Belg. 1896, 732).

6. 1 mol. of ethylene dichloride, 5 vols. of methyl alcohol and 3 mols. of sodium formate are heated together at 165°–170° in an autoclave for 7 hours. After cooling, the methyl alcohol is separated and distilled at ordinary pressure, the glycol under reduced pressure (Brooks and Humphrey, J. Ind. Eng. Chem. 1917, 9, 750).

Glycol is a colourless, odourless, syrupy liquid with sweet taste, miscible with alcohol and water, but almost insoluble in ether. 100 parts ether dissolve 1·1 part of glycol (Knorr, Ber. 30, 912). It dissolves NaCl, $ZnCl_2$, and many other chlorides; also K_2CO_3, KOH, and $Ca(OH)_2$.

By action of oxidising agents, e.g. platinum black, it forms glycollic acid. Nitric acid converts it into glycollic acid, glyoxylic acid, and oxalic acid (Debus, Annalen, 110, 316). Heated with solid KOH to 250°, glycol yields potassium oxalate and hydrogen (Wurtz). Heated with large quantity of water at 200°–210° yields aldehyde (Nevole, Bull. Soc. chim. [ii.] 25, 289); $ZnCl_2$ at 250° decomposes glycol into aldehyde, crotonaldehyde, and water. By electrolysis of an acid (H_2SO_4) solution of glycol, formic acid, formaldehyde, CO_2, traces of a sugar and a non-volatile acid, not glycollic, are formed. (Löb and Pulvermacher, Zeitsch. Elektrochem. 1910, 16, 1). Chlorine forms a crystallisable halogen compound, m.p. 39°, b.p. 200°; and an oily body, $C_6H_{12}O_4$, b.p. 240° (Mitscherlich, J. 1863, 485). H_2O_2 in presence of ferrous compounds yields glycollic aldehyde (Fenton and Jackson, Chem. Soc. Trans. 1899, 75). Heated with aldehydes, glycol yields ethylene oxide derivatives, e.g. glycol and œnanthaldehyde; heated at 125°–130° for some days yield ethylene œnanthylidene oxide

$$C_6H_{13}\cdot CH<^{OCH_2}_{OCH_2}$$
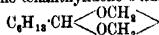
b.p. 180°; similarly, valeraldehyde and propaldehyde yield $C_4H_9\cdot CH<^{OCH_2}_{OCH_2}>$, b.p. 142°;

and $C_2H_5\cdot CH<^{OCH_2}_{OCH_2}>$, b.p. 105°–107°, respectively (Lochert, Bull. Soc. chim. [4] 3, 337, 716). With Na and EtI, yields glycol monoethyl ether, a liquid boiling under 748 mm. at 134·8°, and having a density of 0·93535 at 15°/15° (Palomaa, Ber. 42, 3873).

Glycol is converted into glycollic acid by the action of Bacterium aceti, provided the acid be neutralised (e.g. by $CaCO_3$) as fast as formed, otherwise after a short time the glycollic acid formed stops the further action (A. J. Brown, Chem. Soc. Trans. 51, 638). NH_4Cl and glycol at 300°–400° form collidine $C_8H_{11}N\cdot HCl$ (Hofmann, Ber. 17, 1905). Phosgene gas at ordinary temperatures converts glycol into glycol carbonate $CO(OCH_2)_2$ (with liberation of HCl), a stable compound, soluble in water, alcohol, and ether, and crystallising in colourless needles (Nemirowsky, J. pr. Chem. [2] 28, 439). Heated with strong formic acid for some time (Henninger, Ber. 7, 263), or with oxalic acid (Lorin, Bull. Soc. chim. [ii.] 22, 104), gives glycol diformin $C_2H_4(CH_2O)_2$, b.p. 174°; in the latter case formic acid is also produced. With mineral acid or dehydrating agents yields acetaldehyde, ethylidene ethylene ether and chiefly diethylene ether $O<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>O$ (Faworsky, J. Russ. Phys. Chem. Soc. 1906, 38, 741). By action of sodium on glycol, we get sodium ethylenate $C_2H_4(OH)ONa$, a white crystalline deliquescent body, which, on heating to 190° with more sodium yields disodium ethylenate, a deliquescent mass. The former, with C_2H_5Br in a sealed tube, yields ethylene, glycol, NaBr, and probably $NaCHO_2$ (Wurtz).

De Coninck (Bull. Acad. Roy. Belg. 1905, 360) distinguishes between glycol and glycerol as follows. Uranyl sulphate is dissolved in a small quantity of water, excess of ethylene glycol added, the whole placed in a flask and exposed to sunlight. In 2 hours the liquid is quite green, and in 2½ hours uranous sulphate is precipitated. With glycerol no such colouration or precipitation takes place.

Glycol forms a number of cyclic esters and cyclic compounds analogous to the metallic saccharates (Bischoff, Ber. 40, 2803; Grün and Bockisch, ibid. 40, 2812).

2. Diethylene glycol

$$HO\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot OH$$
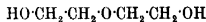
b.p. 250°, sp.gr. 1·132 at 0°; V.D. = 3·78 at 311° (calc. 3·67) (Lourenço, Ann. Chim. Phys. [3] 67, 275); from ethylene oxide and water, or better, ethylene oxide and glycol at 100° (Wurtz); from glycol and ethylene bromide or bromhydrin at 115°–120° (Lourenço); by action of glycol monoacetate upon sodium glycol at 130°–140° (Mohs, Zeitsch. Chem. 1866, 495).

An oily liquid, soluble in water, alcohol, and ether; concentrated HI at 100° forms $C_2H_4I_2$; oxidised by HNO_3 to glycollic acid, oxalic acid, and diglycollic acid $C_4H_6O_5$. The chlorhydrin $C_4H_9O_2Cl$, b.p. 180°–185° (L.), 190°–200° (W.), is formed by leading HCl into ethylene oxide, or from ethylene oxide and ethylene chlorhydrin at 140° (Wurtz, Ann. Chim. Phys. [3] 69, 338). 1 molecule ethylene chlorhydrin and 2 molecules glycol are heated at 140°, saturated with HCl

and again heated at 100° (Lourenço, *ibid.* [3] 67, 290), a liquid soluble in water.

The *bromhydrin*, b.p. 205°, is prepared from glycol and ethylene bromide at 160° (L.).

3. Tri-ethylene glycol

$$C_6H_4(OH)\cdot O\cdot C_2H_4\cdot O\cdot C_2H_4OH$$
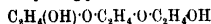
b.p. 290°; sp.gr. 1·138; a liquid miscible with alcohol and water, and oxidised by HNO_3 to *diglycol-ethlenic acid* $C_6H_{10}O_6$ (Lourenço; Wutrz).

The *chlorhydrin* $C_6H_{13}O_3Cl$: b.p. 222°-232°; is a liquid soluble in water (L.).

The *bromhydrin* $C_6H_{13}O_3Br$; b.p. (with decomposition) 250° (L.).

4. Tetra-ethylene glycol $C_8H_{17}O_5$; b.p. 230° at 25 mm. (L.; W.).

The *chlorhydrin* $C_8H_{17}O_4Cl$; b.p. 262°-272°; is soluble in water (L.).

5. Penta-ethylene glycol $C_{10}H_{22}O_6$; b.p. 281° at 25 mm.; a viscid liquid soluble in water, alcohol, and ether (L.).

6. Hexa-ethylene glycol $C_{12}H_{26}O_7$; b.p. 325° at 25 mm.; a very viscid liquid (L.).

Ethylene bromide $C_2H_4Br_2$ or $CH_2Br\cdot CH_2Br$; m.p. 9·975° (Moles, Anal. Fis. Quim. 1912, 10, 131), 10·012° (Biron, Zeitsch. physikal. Chem. 1913, 81, 590); b.p. 131·6° (R.), 129·5° at 745 mm. (Anschütz, Annalen, 221, 137), 130·39° (corr.) (Thorpe and Rodger); sp.gr. 2·1804 at 20° (Biron, *l.c.*), 2·2132 at 0°/4°, 2·1901 at 10·9°/4° (Thorpe. Chem. Soc. Trans. 37, 177); by action of C_2H_4 and Br (Balard, Ann. Chim. Phys. [2] 32, 375); formed together with ethylidene bromide CH_3CHBr_2 by heating C_2H_5Br with Br to 180° (Tawildarow, Annalen, 176, 14). From C_2H_4Cl, Br, and iron wire at 100° (V. Meyer and Petrenkò, Ber. 25, 3307); also from C_2H_5Br, Br, and $AlBr_3$ at 65°-70° (Mouneyrat, Bull. Soc. chim. [iii.] 19, 497).

Preparation.—1. Ethylene, purified by passing through H_2SO_4 and NaOH solution, is led into bromine covered with water, contained in a wide tube, until the colour of the Br disappears; the product is washed with NaOH and water, dried by $CaCl_2$ and distilled (Erlenmeyer and Bunte, Annalen, 168, 64; Erlenmeyer, *ibid.* 192, 244; Prideaux, Chem. News, 1916, 113, 277). 2. By heating together at 150° in glacial acetic acid glycol diacetate and HBr, a quantitative yield of $C_2H_4Br_2$ is obtained (Perkin and Simonsen, Chem. Soc. Trans. 1905, 856).

Is a colourless mobile liquid with a pleasant smell and sweet taste; V.D. 6·485 (Regnault). When heated with water to 150°-160°, it yields, first glycol, and, on longer heating, HBr and aldehyde (Carius, Annalen, 131, 173). Zn acts upon an alcoholic solution of $C_2H_4Br_2$ with formation of C_2H_4 and $ZnBr_2$ (Gladstone, Ber. 7, 364); by heating with KI and water, ethane is produced. Alcoholic KOH yields C_2H_3Br, and in excess C_2H_2. Heated with $AlBr_3$ at 100°-110°, yields C_2H_2 and $C_2H_2Br_4$; with Cl and $AlCl_3$, yields C_2Cl_6 (Mouneyrat).

Aqueous KOH produces, after long contact, C_2H_3Br (Stempnevsky, Annalen, 192, 240). By heating with strong NaOH and KOH solution, glycol and C_2H_3Br are produced. If $C_2H_4Br_2$ be heated with excess of H_2O and PbO to 220°, aldehyde is formed (due to decomposition of $C_2H_4(OH)_2$, first formed, into C_2H_4O and H_2O) (Eltekow, Ber. 6, 558, and Nevole, *ibid.* 9, 447).

Heated with strong HI solution, yields $C_2H_4I_2$ (Sororkin, Zeitsch. Chem. 1870, 519). Heated with Ag_2O and water, aldehyde is produced, and when heated with Ag_2CO_3 and water, yields glycol (Beilstein and Wiegand, Ber. 15, 1368). Treated with Ag_2SO_4 and benzene, yields dibromethyl sulphate $(C_2H_4Br)_2SO_4$; with Ag_2SO_4 and water, bromethyl sulphuric acid $(C_2H_4Br)HSO_4$ (B. and W.).

Bromethylene bromide $CH_2Br\cdot CHBr_2$; b.p. 186·5° (Wurtz, Annalen, 104, 243), 187°-188° at 721 mm. (Denzel, *ibid.* 195, 202), 191° (Tawildarow, *ibid.* 176, 22), 73° at 11·5 mm., 83° at 18 mm., 187°-188° at 751·5 mm. (Anschütz, *ibid.* 221, 138); sp.gr. 2·624 at 16° (T.), 2·620 at 23° (W.), 2·6189 at 17·5°/4°, 2·6107 at 21·5°/4° (A.).

Prepared from monobromethylene and Br (Wurtz); from C_2H_3I and Br (Simpson, J. 1857, 461); from C_2H_3Br and Br at 170° (Hofmann, J. 1860, 364); or from $C_2H_4Br_2$ and Br at 200° (Tawildarow); decomposed by $KC_2H_3O_2$ at 150°, or by H_2O and PbO into dibromethylene and HBr. C_2H_5NaO yields ethylidene dibromide (Gray, Chem. Soc. Trans. 1897, 1024). Alcoholic KOH gives $C_2H_3Br_2$, C_2H_2, and bromacetylene C_2HBr. When heated with excess of absolute alcohol, C_2H_5Br and probably C_2H_3BrO bromaldehyde, are formed (Glöckner, Annalen, Suppl. 7, 110).

The isomeric body CH_3CBr_3 is not known.

Dibromethylene dibromide $C_2H_2Br_4$. Two isomerides are known.

1. *Acetylidene tetrabromide*; $CH_2Br\cdot CBr_3$ boils with decomposition at 200°; b.p. 103·5° at 13·5 mm.; sp.gr. 2·9292 at 17·5°/4°, 2·9216 at 21·5°/4° (Anschütz, Annalen, 221, 140). Formed from *as*-dibromethylene $CH_2 : CBr_2$ and bromine (Lennox, *ibid.* 122, 124; Chem. Soc. Trans. 1862, 206; Reboul, Annalen, 124, 270). From C_2H_5Br and Br at 180° a compound $C_2H_2Br_4$ is produced, which boils with decomposition at 208°-211° (Tawildarow). By heating a mixture of pyrotartaric acid and bromine with water at 150° (Bourgoin, Ann. Chim. Phys. [5] 12, 427).

2. *Acetylene tetrabromide* $CHBr_2CHBr_2$; b.p. 137°-137·2° at 36 mm., 114° at 12 mm., at 15 mm. 124°-126°, at 54 mm. 151°; sp.gr. 2·9710 at 17·5°/4°, 2·9629 at 21·5°/4° (Anschütz, Ber. 12, 2974, and Annalen, 221, 139); decomposes at 190° into HBr, Br, and C_2HBr_3.

By leading C_2H_2 into bromine covered with water (Reboul, Annalen, 124, 269; Berthelot, Bull. Soc. chim. [ii.] 5, 97); the crude $C_2H_2Br_4$ is then reduced by means of alcohol and Zn dust to $C_2H_2Br_2$, when the admixed $C_2H_3Br\cdot Br_2$ is converted into C_2H_2Br; the $C_2H_2Br_2$ is then purified by distillation and treated with bromine (Anschütz, Annalen, 221, 139); by action of Br and $AlBr_3$ at 105°-110° upon $C_2H_4Br_2$ (Mouneyrat, Bull. Soc. chim. [iii.] 19, 498). A liquid smelling of camphor and chloroform; decomposed by heating or by action of Na; by heating with alcoholic KOH, C_2H_2 and C_2HBr are produced. Cl produces $C_2Cl_4Br_2$ (Bourgoin, Bull. Soc. chim. [i.] 23, 4); when heated with Br and water to 180°, yields C_2Br_4 and C_2Br_6 (Anschütz); with C_6H_6 and $AlCl_3$, produces anthracene; heated with aniline, dimethylaniline, or alcoholic NH_3, yields $NHBr : CBr_2$.

Pentabromethane $CHBr_2\cdot CBr_3$; m.p. 56°-57°

(Bourgoin), 54° (Denzel, Ber. 12, 2208), 48°–50° (Reboul); boils with decomposition at 210° (at 300 mm.) (Denzel). From C_2HBr_3 (Elbs and Newmann, J. pr. Chem. [2] 58, 254; Lennox, Annalen, 122, 125) or C_2HBr (Reboul, *ibid.* 124, 268) and bromine. By slow oxidation (by exposure to air) of C_2HBr_3 (Demole, Bull. Soc. chim. [ii.] 34, 204); from $C_2H_3Br_4$ and Br at 165° (Bourgoin, *ibid.* 23, 173). Forms prismatic needles soluble in alcohol and ether.

Perbromethane C_2Br_6 *v.* CARBON TRIBROMIDE.

Ethylene bromolodide; m.p. 28°; b.p. 163°; sp.gr. 2·516 at 29°. From C_2H_3Br and conc. HI at 100° (Reboul, Annalen, 155, 213). From C_2H_4 and 1Br (Simpson, J. 1874, 326). Needles, with alcoholic KOH yields, in the cold, C_2H_3I and HBr, and on warming HBr, HI, and C_2H_2. Forms iodoform with alcoholic CH_3COOK at 100°.

Ethylene bromhydrin $C_2H_4Br·OH$, *Glycol bromhydrin*; b.p. 150°–152°, at 18 mm. 63°–64° (Henry, J. 1889, 1321), 155° (Lourenço, Ann. Chim. Phys. [3] 67, 287); sp.gr. 1·66 at 8° (H.); sp.gr. 1·7195 at 18·6° (H.). From glycol and $C_2H_4Br_2$ at 115°–120° (Lourenço); from glycol and HBr at 100°, and from $CH_2I·CH_2OH$ and bromine (Henry); also from 3 mols glycol and 1 mol. PBr_3 (Demole, Ber 9, 48); from ethylene and HBrO (60 p.c.) (Mokiewsky, J. Russ. Phys. Chem. Soc. 30, 900); with zinc-dust and alcohol is reduced to C_2H_4; together with ethylene dibromide by the action of ethylene on bromine water (Read and Williams, Chem. Soc. Trans. 1917, 111, 240)

Ethylene dichloride, *Elayl chloride*, *Dutch liquid* CH_2ClCH_2Cl; b.p. 84·9° (Pierre, J. 1847–48, 63), 83·5° (corr.) (Thorpe, Chem. Soc. Trans 37, 182), 84·5°–85° at 750·9 mm. (Bruhl, Annalen, 203, 10), 83·3° at 749 mm. (R. Schiff, *ibid.* 220, 96), 84·1° at 760 mm. (Städel, Ber. 15, 2563); sp.gr. 1·2808 at 0°/4° (Thorpe), 1·2803 at 0° (Pierre), 1·2562 at 20° (Haagen, Bull. Soc. chim. ii. 10, 355), 1·2656 at 9·8°/4°, 1·1576 at 83·3°/4° (R. Schiff), 1·2606 at 14·4°, 1·204 at 62·5° (Landolt and John); b.p 83·93° (corr.) (Thorpe and Rodger) refractive index; at $t°$ $\mu_A = 1·441466 - 0·000446t$, mol. refract. $= 34·06$ (Kanonnikow); capill. constant at b.p. $a^2 = 4·198$ (R. Schiff, Annalen, 223, 72). By action of C_2H_4 upon Cl (Deiman, Trootswyk, Bondt, and Lauwerenburgh, Crell's Ann. 1795, 2, 200); by leading C_2H_4 into $SbCl_5$ or into molten $CuCl_2$ (Wöhler, Pogg. Ann. 13, 297); from C_2H_4Cl and $SbCl_5$ at 100° (V. Meyer and Müller, J. pr. Chem. [ii.] 46, 173); also by action of glycol upon PCl_3 (Wurtz) or upon HCl at 100° (Schorlemmer, Chem. Soc. Trans. 1881, 1); from ethylene diamine and NOCl in carefully cooled *m*-xylene solution (Solonina, J. Russ. Phys. Chem. Soc. 30, 606). Prepared best according to Limpricht's method (Annalen, 94, 245). Ethylene is passed into a gently heated mixture of 2 parts manganese dioxide, 3 parts common salt, 4 parts water, and 5 parts sulphuric acid, and when the mass turns yellow it is distilled. It can be prepared in good yield from ethylene and chlorine if the temperature is kept at 0°; at higher temperatures considerable quantities of trichloroethane are formed. It forms an oily liquid, insoluble in water. When heated with alcoholic KOH, it yields KCl and C_2H_3Cl, and with K it forms H_2, KCl, and C_2H_3Cl

(Liebig, Annalen, 14, 37). Heated with $AlCl_3$ to 80°–85° is decomposed into HCl and C_2H_2 (Mouneyrat, Bull. Soc. chim. [iii.] 19, 446). With NH_3 it forms bases, $N_2H_4C_2H_4$, $N_2H_2(C_2H_4)_2$, &c. With ethylamine, it yields *collidine* (*trimethylpyridine* $C_5H_2(CH_3)_3N$), C_2H_5Cl, and also NH_3 and $N(C_2H_5)_3$ (Hofmann, Ber. 17, 1907).

Chlorethylene $CH_2:CHCl$, *Vinyl chloride*; at ordinary temp. a gas; b.p. $-18°$ to $-15°$; by action of alcoholic KOH upon ethylene chloride (Regnault, Annalen, 14, 28), or ethylidene chloride (Wurtz and Frapolli, *ibid.* 108, 224). To prepare it the ethylene dichloride and alcoholic potash are left in contact for 3 or 4 days in the cold, and the mixture is then warmed. Combines with Cl to form $C_2H_3Cl_3$. Polymerises in sunlight, and forms a solid insoluble mass of sp gr. 1 406 (Baumann, Annalen, 163, 317).

Dichlorethylene $C_2H_2Cl_2$.

1. *Dichlorethylene* $CH_2:CCl_2$; b.p. 33·5°–35° (Joetlsch and Faworsky); b.p. 37° (Kramer, Ber. 3, 261); sp.gr. 1·250 at 15°, obtained by action of alcoholic KOH upon $CH_2Cl·CHCl_2$ (Regnault, J. pr. Chem. [ii.] 18, 80). Also by action of Zn shavings in alcoholic solution upon the trichlorethyl ester of acetic acid (Joetlsch and Faworsky, J Russ. Phys. Chem. Soc. 30, 998). Polymerises easily into a solid amorphous insoluble body.

2. *Sym-Dichlorethylene* (*Acetylene dichloride*) $CHCl:CHCl$; b.p. 55°; by distillation of the compound of C_2H_2 with $SbCl_5$ (Berthelot and Jungfleisch, Annalen, Suppl. 7, 253); also by action of Zn upon an alcoholic solution of $CHClBr·CHClBr$, or by leading C_2H_2 into aqueous solution of ICl (Sabanejeff, Annalen, 216, 262).

Trichlorethylene $CHCl:CCl_2$; b.p. 87·4°–87·55°; sp.gr. 1·4904 at 4°/4°, 1·4598 at 25·5°/25·5° (Veley, Proc. Roy. Soc. 1910, B 82, 217), 85·8°–86·0°/741·6 mm., m.p. $-83°$, D_4^{20} 1·4649; D_4^{15} 1·4695 (Erdmann, J. pr. **Chem.** 1912, ii. 85, 78). From isomeric compounds $C_2H_2Cl_4$, and alcoholic KOH (Berthelot and Jungfleisch); also by action of nascent H (Zn and H_2SO_4) upon C_2Cl_6 (Fischer, J. 1864, 481): from anhydrous chloral and P_2S_5 at 160°–170° (Paternò and Oglialoro, Ber. 7, 81); combines with Cl to form C_2HCl_5. By action of ammonia in aqueous solution on tetrachloroethane (Comp. prod. chem. d'Alais; Eng. Pat., 132755).

For observations on its autoxidation, *see* Erdmann (*l c.*).

Tetra-chlorethylene C_2Cl_4 *v. Carbon dichloride*, art. CARBON *Cf.* Weiser and Wightman, J. Phys. Chem. 1919, 23, 415.

Hexachlorethane C_2Cl_6 *v.* Carbon trichloride, art. CARBON.

Ethylene chlorhydrin $HO·CH_2·CH_2Cl.$ *Chlorethyl alcohol*, *Glycol chlorhydrin*; b.p. 128° (Wurtz, Annalen, 110, 125), 132°; 51°–52° at 22 mm.; sp.gr. 1·2005 at 18·6° (Henry, J. 1889, 1321), 1·24 at 8°. From glycol and HCl (gas) at 100° (W.). If excess of HCl be used, $C_2H_4Cl_2$ is produced (Schorlemmer, Chem. Soc. Trans. 39, 143); from glycol and Cl_2S_2 (Carius, Annalen, 124, 257); from C_2H_4 and ClOH (Carius, *ibid.* 126, 197; Butlerow, *ibid.* 144, 40). Dry HCl is led into glycol kept at 148°; the $C_2H_4Cl(OH)$ distils off (Ladenburg, Ber. 16, 1408). A liquid miscible with water;

yields alcohol with Na amalgam and H_2O (Lourenço, Annalen, 120, 92). Oxidised by CrO_3 to chloracetic acid (Kriwaxin, Zeitsch. Chem. 1871, 265); with KOH, yields ethylene oxide. *Cf.* Gomberg, J. Amer. Chem. Soc. 1919, 41, 1414.

Ethylene chlorobromide $CH_2Cl\cdot CH_2Br$; b.p. 107°–108° (Leeocœur, Bull. Soc. chim. [ii.] 29, 484); sp.gr. 1·79 at 0° (L.), 1·705 at 11° (Montgolfier and Giraud, *ibid.* 33, 12), 1·689 at 19°. By action of Br upon $CH_2Cl\cdot CH_2I$ (Henry, Annalen, 156, 14); from $C_2H_4Br_2$ and $SbCl_5$ (Lössner, J. pr. Chem. [2] 13, 421) or $C_2H_4Br_2$ and $HgCl_2$ at 150°–180° (M. and G.); by action of Br upon $C_2H_4Cl(OH)$ at 130° (Demole, Ber. 9, 556). To prepare it, first chlorine and then ethylene is passed into Br, kept under a mixture of equal vols. of strong HCl and water (James, J. pr. Chem. [2] 26, 380; also Simpson, Proc. Roy. Soc. 27, 118); decomposed by alcoholic KOH, with formation of C_2H_3Cl.

Ethylene chloroiodide $CH_2Cl\cdot CH_2I$; m.p. −15·6° (Sehn der, Zeitsch. physikal. Chem. 19, 157), b.p. 140° (Sorokin, Zeitsch. Chem. 1870, 519), 140·1° (corr.) (Thorpe, Chem. Soc. Trans. 37, 189), 137°–138° (Meyer and Wurster, Ber. 6, 964); sp.gr. 2·151 at 0° (S.), 2·16439 at 0°, 2·13363 at 15·3°/0° (T.). From $CH_2I\cdot CH_2I$ and ICl; from C_2H_4 and an aqueous solution of ICl (Simpson, Proc. Roy. Soc 12, 278). Decomposed by alcoholic KOH and HI and C_2H_3Cl; nascent H yields HCl, HI, and C_2H_4; moist Ag_2O at 160° produces glycol (Simpson). Finely divided silver at 160° yields C_2H_4 and $C_2HCl\cdot CH_2Cl$ (Friedel and Silva, Bull. Soc. chim. [ii.] 17, 242). Heated with HI solution, yields C_2H_5I and $C_2H_4I_2$ (Sorokin).

Ethylene cyanhydrin $HO\cdot CH_2\cdot CH_2CN$; b.p. 220°–222° at 723·5 mm.; sp.gr. 1·0588 at 0°. By long digestion of C_2H_4O (ethylene oxide) with anhydrous HCN at 50°–60° (Erlenmeyer, Annalen, 191, 273); miscible with alcohol and water; 100 parts ether dissolve 2·3 parts $C_2H_4(OH)CN$ at 15°; insoluble in CS_2. Forms a chloride with PCl_5, which boils at 174°–176° under 752 mm., and has sp.gr. 1·443 at 18·5° (Henry, Bull. Acad. Roy. Belg. iii. 35, 360).

Ethylene cyanide $C_2H_4(CN)_2$, *Succinonitrile*; m.p. 54·5° (Ngvole and Tscherniak, Bull. Soc. chim. [ii.] 30, 101), 51°–52° (Henry, *ibid.* 43, 618); b.p. 158°–160° at 20 mm. (Pinner, Ber. 16, 360), 265°–267° (H.); sp.gr. 1·023 at 45°. By heating on a water-bath $CH_2Br\cdot CH_2Br$ with KCN and alcohol (sp.gr. 0·84) (Simpson, Proc. Roy. Soc. 10, 574); the liquid is filtered from the KBr, and distilled, when the alcohol is first removed; then the distillation is conducted under diminished pressure; also is produced by electrolysis of potassium cyanacetate (Moore, Ber. 4, 520); is a white amorphous mass soluble in water, chloroform, and alcohol; slightly in carbon disulphide and ether; decomposed when distilled at ordinary pressure. Decomposed by heating with KOH or HCl into NH_3 and succinic acid; with $AgNO_3$ forms plates of $C_2H_4(CN)_2\cdot 4AgNO_3$, which is soluble in water and alcohol, and explodes when heated (Simpson).

Ethylene diamine $NH_2\cdot C_2H_4\cdot NH_2$; m.p. 8·5° (Kraut, Annalen, 212, 263), b.p. 116·5°; sp.gr. 0·9002 at 15° (Kraut). By heating $C_2H_4Cl_2$ or $C_2H_4Br_2$ with alcoholic NH_3 to 100° (Cloëz, J. 1853, 468); by distillation of $\alpha\beta$-diaminopropionic acid (Neuberg and Neimann, Zeitsch. physikal. Chem. 45, 110); by treatment of $C_2H_4(CN)_2$ with Sn and HCl (Fairley, Annalen, Suppl. 3, 372). 42 grams of $CH_2Cl\cdot CH_2Cl$ and 510 c.c. aqueous NH_3 are heated for 5 hours to 115°–120° in a sealed tube; the product is then evaporated until it begins to crystallise, and is then precipitated with 3 times its volume of absolute alcohol; the precipitated $C_2H_4(NH_2)_2,2HCl$ is then washed with alcohol and the base set free by distillation with powdered NaOH (Kraut, *l.c.*; also Hofmann, Ber. 4, 666). The by-product from the manufacture of chloral, consisting of $CH_2Cl\cdot CH_2Cl$, $CH_3\cdot CHCl_2$, &c., can be used. A thick oily liquid, with faint ammoniacal smell, soluble in water, not miscible with ether or benzene; the aqueous liquid, which contains $C_2H_4(NH_2)_2,H_2O$, cannot be freed from water by BaO, but only by distillation over Na. Caro's acid oxidises it to glyoxime (Bamberger and Seligman, Ber. 36, 3831). With HClO and HBrO, yields tetrachloro and tetrabromo derivatives; *e.g.* $Br_2N\cdot C_2H_4\cdot NBr_2$ (Chattaway, Chem. Soc. Trans. 1905, 381). Decomposed by HNO_2 into ethylene oxide and oxalic acid (Hofmann, J. 1859, 386); is a strong base and forms salts; combines with CS_2 to form crystals of
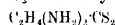
$$C_2H_4(NH_2)_2\cdot CS_2$$

soluble in water, insoluble in alcohol and ether. $C_2H_4(NH_2)_2,2HCl$, long silvery needles insoluble in alcohol. $C_2H_4(NH_2)_2HCl,PtCl_4$, yellow leaflets, slightly soluble in water (Greiss and Martius, Annalen, 120, 327); $C_2H_4(NH_2)_2(HCNS)_2$, large prisms, very soluble in water, m.p. 145° (Hofmann, Ber. 5, 245). Forms many compounds with metallic salts and a periodide $C_2H_4(NH_2)HI\cdot I_4$, which melts at 218°.

Diethylene diamine, *Piperazine*

$$(C_2H_4)_2(NH)_2 \text{ or } C_2H_4\!<\!\!\begin{array}{c}NH\\NH\end{array}\!\!>\!C_2H_4$$
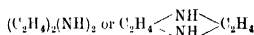
m.p. 104° (Berthelot); b.p. 170° (Hofmann, J. 1858, 343), 145°–146° (Berthelot), 140° (Rosdalsky). From ethylene chloride and alcoholic NH_3 (Cloez; Hofmann, Natanson, Annalen, 98, 291); from sodium ethylene glycollate and acid derivatives of ethylene diamine by heating at 250°–350° (D. R. P. 67811); by heating the sodium compound of *sym*-diacyl ethylene diamine with anhydrous glycol or ethylene bromide at 200° (D. R. P. 73354); by reduction of ethylene oxamide with zinc-dust and KOH (D. R. P. 66461). (For other methods of preparation, *see* D. R. P. 70055, 70056, 73125, 74628, 79121, 9803, 100232.)

Forms a hydrate $C_4H_{10}N_2,6H_2O$; m.p. 44° (Berthelot). Piperazine is not changed by heating with HCl or H_2SO_4 at 200°. With carbonyl chloride it forms tricarbonyl piperazine. It forms a periodide $C_4H_{10}N_2\cdot 2HI\cdot I_4,3H_2O$, m.p. 283°. The anhydrous periodide melts at 280° (Herz, Ber. 30, 1585). Piperazine reacts with 2 molecules HBrO to form an additive compound, which, on treatment with dilute alkali or piperazine solution, yields *n*-dibromopiperazine. This latter can form an additive compound with 2 molecules of HBrO (Chattaway, Chem. Soc. Trans. 1905, 951). Piperazine reacts

with an excess of EtI at temperature of water-bath to form triethyl piperazonium iodide; m.p. 240°. Colourless needles, insoluble in cold water, ligroin, C_2Cl_3, C_6H_6, and CS_2; soluble in warm alcohol (Van Rijn, Chem. Zentr. 1898, 1, 727) (v. *Piperazine*).

sym.Diethylene diethyldiamine

$$(C_2H_4)_2(NH \cdot C_2H_5)_2, H_2O$$
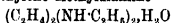
b.p. 165° (Schmidt and Wichmann, Ber. 24, 3247); from $(C_2H_4)_2(NH_2)_2$ and C_2H_5I, or from $C_2H_4Br_2$ and $NH_2 \cdot C_2H_5$ (Hofmann, J. 1859, 389); from piperazine and an excess of $KEtSO_4$ in aqueous solution (Van Rijn, Chem. Zentr. 1898, i. 727). It combines with salts of Cd, Cr, Zn, and Ni.

as.Diethylene diethyldiamine

$$NH_2 \cdot C_2H_4 \cdot N(C_2H_5)_2$$
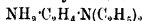
mobile liquid; b.p. 145°; sp.gr. 0·827 at 18·5°/18·5°; from bromethylphthalimide and diethyl-amine with subsequent hydrolysis, yields a *platinochloride*, m.p. 230°; an *aurochloride*, m p. 161°–163°; and a *picrate*, m.p. 211° (Ristenpart, Ber. 1896, 29. 2526).

Triethylene diamine $(C_2H_4)_3N_2$; b.p. 210°; soluble in water (Hofmann, J. 1858, 343; Harries, Annalen, 294, 350).

Diethylene triamine

$$NH_2 \cdot C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH_2$$

b.p. (with slight decomposition) 208°; formed with other products by action of NH_3 upon $C_2H_4Br_2$; the double salt with $PtCl_4$ being less soluble than that of triethylene triamine, it can be separated from that body (Hofmann, J. 1861, 514).

A strongly alkaline liquid miscible with water and alcohol. Its salts are soluble in water, less so in alcohol, $2[(C_2H_4)_2N_3H_5, 3HCl]3PtCl_4$ forms golden-yellow needles.

Triethylene triamine

$$C_2H_4 \begin{array}{c} \diagup NH \cdot C_2H_4 \diagdown \\ \diagdown NH \cdot C_2H_4 \diagup \end{array} NH$$
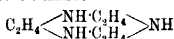
b.p. 216° (Hofmann, J. 1861, 514); forms salts; $[(C_2H_4)_3N_3H_5, 3HCl]_2PtCl_4$: long golden-yellow needles moderately soluble in water; with hydrobromic acid gives $(C_2H_4)_3N_3H_5, 3HBr$ from acid solutions: from weaker acid solution $(C_2H_4)_3N_3H_5, 2HBr$.

Tetraethylene triamine $(C_2H_4)_4N_3H_5$; by action of alcoholic NH_3 upon $C_2H_4Br_2$ (Hofmann, Ber. 3, 762); forms 3 series of salts with 1, 2, or 3 molecules of monobasic acid; the hydrobromides are amorphous bodies, almost insoluble in water, alcohol, and ether.

Triethylene tetramine

$$NH_2 \cdot C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH_2$$

m.p. +12°; b.p. 266°–267°; sp.gr. 0·9817 at 15°; a strongly alkaline syrup from $C_2H_4Cl_2$ and $C_2H_4(NH_2)_2$, or from $C_2H_4Br_2$ and alcoholic NH_3 (Hofmann, J. 1861, 519); yields

$$C_6H_{18}N_4 \cdot 4HCl \cdot 2PtCl_4$$
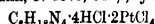
a yellow amorphous powder almost insoluble in water.

Ethylene diformin $C_2H_4(CHO_2)_2$; b.p. 174°; by heating glycol with pure formic acid (Henninger, Ber. 7, 263); also by heating oxalic acid with glycol (Lorin, Bull. Soc. chim. [ii] 22, 104). Decomposed when heated at 200° in sealed tube into CO_2, CO, H_2O, and C_2H_4.

Ethylene ferrous chloride $C_2H_4FeCl_2, 2H_2O$; by heating $FeCl_2$ and ether to 150° (Kachler, Ber. 2, 510); forms prisms fairly soluble in water. The corresponding compound

$$C_2H_4FeBr_2, 2H_2O$$
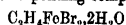
is prepared by leading C_2H_4 into a strong aqueous solution of $FeBr_2$ in sunlight (Chojnacki, Zeitsch. Chem. 1870, 420); forms light-green deliquescent crystals.

Ethylene iodide $CH_2I \cdot CH_2I$; m.p. 81°–82° (Aronstein and Kramps, Ber. 13, 489); sp.gr. 2·07; from C_2H_4 and I in sunlight (Faraday, Gm. 4, 682), also in the shade, especially if warmed (Regnault, Annalen, 15, 67); a mixture of I and alcohol (absolute) is saturated with C_2H_4 with repeated agitation (Semenow, J. 1864, 483).

Crystalline plates or prisms decomposed by heating; when warmed with alcohol to 70°, $IC_2H_4 \cdot OC_2H_5$, is produced; $HgCl_2$ gives in the cold C_2H_4ICl, and on heating $C_2H_4Cl_2$ (Maumené, J. 1869, 345); alcoholic KOH converts it into C_2H_3I (Regnault, Annalen, 15, 63).

Ethylene iodohydrin $CH_2I \cdot CH_2OH$; from $C_2H_4(OH)_2$ and gaseous HI (Simpson, *ibid.* 113, 121); also by heating $C_2H_4(OH)Cl$ with KI (Butlerow and Ossokin, *ibid.* 144, 42).

An oil, b.p. 85°/25 mm.; sp.gr. 2·1649 at 18·6° (Henry, Ber. 24 Ref. 75).

Ethylene nitrate $NO_3CH_2 \cdot CH_2NO_3$; b.p. 114°–116° with explosion (Demjanow, Chem. Zentr. 1899, i. 1064); sp.gr. 1·5099 at 4°, 1·4960 at 15°, 1·4860 at 25° (Perkin). Is formed when glycol is treated with HNO_3 and H_2SO_4, also by interaction of C_2H_4 and N_2O_5 in the cold (Demjanow); an oily liquid which is inflammable, explodes on percussion, and is poisonous; KOH converts it into alcohol (Henry, Ber. 3, 529; also Champion, Compt. rend. 73, 571). On reduction yields CH_3CHO, $C_2H_4(NH_2)_2$, and $H_2N \cdot CH_2 \cdot CH_2OH$.

Ethylene nitrite

$$C_2H_4(NO)_2 \text{ or } NO_2 \cdot CH_2CH_2 \cdot NO$$
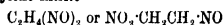
m.p. below −15°; b.p. 96·8°; sp.gr. 1·2156 at 0° (Bertoni). Is prepared by distilling glycerol trinitrate with more than an equivalent amount of glycol. Soluble in alcohol to form C_2H_5ONO (Bertoni, Gazz. chim. ital. 15, 353); insoluble in and slowly decomposed by water.

Nitroethylene can be prepared in 50 p.c. yield by the dehydration of β-nitroethyl alcohol by phosphoric oxide or sodium hydrogen sulphate; an almost colourless mobile liquid, b.p. 98·5°; $D^{13·8}$ 1·073. Vapour violently attacks the eyes and throat. Readily undergoes polymerisation; with alkali the change occurs with explosive violence. Combines with bromine in ethereal solution, yielding nitroethylene dibromide, colourless liquid, b.p. 97°/21 mm. With aniline gives N-β-nitroethyl aniline $NHPh \cdot CH_2 \cdot CH_2 \cdot NO_2$, colourless leaflets, m.p. 37° (Wieland and Sakellarios, Ber. 1919, 52, B, 898).

Ethylene passed into an ice-cold mixture of nitric acid (D 1·4) and concentrated sulphuric acid containing 20 p.c. of sulphur trioxide yields on steam-distillation and fractionation under diminished pressure *ethylene dinitrate*, colourless oil, b.p. 105·5°/19 mm. D^{17} 1·433, and *β-nitroethyl nitrate*, colourless, poisonous oil, b.p.

120-122°/17 mm. D^{15} 1·468. The latter is converted by phosphoric oxide into nitroethylene.

β-Nitroethyl alcohol is a colourless odourless liquid, b.p. 103°/11·5 mm. $D13·3$ 1·309, miscible with water, alcohol, and ether obtained by the action of silver nitrite on ethylene iodohydrin (Wieland and Sakellarios, Ber. 1920, [B] 201.

Ethylene oxide $\begin{matrix} CH_2 \\ \diagdown \\ CH_2 \end{matrix}O$; b.p. 12·5° ; sp.gr.

0·8909 at 4°/4° ; 0·8824 at 10°/10° (Perkin, Chem. Soc. Trans. 1853, 488). From $C_2H_4(OH)Cl$ and KOH (Wurtz, Annalen, 110, 125 ; Ann. Chim. Phys. [3] 69, 317) ; also from $C_2H_4(OH)Cl$ and $C_2H_4(OH)ONa$ (Scheitz, Zeitsch. Chem. 1868, 379) ; also from $C_2H_4I_2$ and Ag_2O at 150° ; from $C_2H_4Br_2$ and Ag_2O at 250° ; or from $C_2H_4Br_2$ and Na_2O at 180° (Greene, J. 1877, 522) ; also by treatment of $C_2H_4Cl(OC_2H_3O)$ with KOH (Demole, Annalen, 173, 125) ; by dropping chlorethylacetate on to a cooled mixture of powdered KOH and sand (Roithner, Monatsh. 15, 666).

A pleasant-smelling liquid miscible with water ; when heated with water in a closed tube, yields glycol, and polyethylene glycol. Has strong basic properties, although not an alkaline reaction. It combines with acids, and precipitates metallic hydroxides from solutions of Mg, Al, Fe, and Cu salts. With Na amalgam forms C_2H_6O. Pt black oxidises it to glycollic acid ; PCl_5 produces $CH_2Cl·CH_2Cl$ (Wurtz, Ann. Chim. Phys. [3] 69, 317, and 355).

Equal molecules of C_2H_4O and Br at 0° form $C_2H_4(OH)Br$, $C_2H_4Br_2$ and other bodies (Demole, Ber. 9, 47), but 2 molecules C_2H_4O and 1 molecule Br, on standing, yield large red or small yellow prisms of $(C_2H_4O)_2Br_2$; m.p. 65° ; b.p. with decomposition at 95° ; they are insoluble in water, but soluble in alcohol. H_2S or contact with Hg separates the Br and leaves dioxyethylene (Wurtz, Ann. Chim. Phys. [3] 69, 321). By long contact with $ZnCl_2$ or KHO, a polymeride which melts at 56° and is insoluble in water, is produced (Wurtz, Bull. Soc. chim. [ii.] 29, 530).

Dioxyethylene, *Diethylene dioxide* $\begin{matrix} CH_2·O·CH_2 \\ | \quad\quad | \\ CH_2·O·CH_2 \end{matrix}$;

m.p. 9° ; b.p. 102° ; sp.gr. 1·0482 at 0°. From $(C_2H_4)_2O_2·Br_2$, and Hg by contact at ordinary temperature. The mixture is then distilled, and distillate rectified over KOH (Wurtz, Ann. Chim. Phys. [3] 69, 323) ; has no marked basic properties, but combines slightly with acetic acid on heating to 120°. Lourenço (*ibid.* [3] 67, 288) obtained it by heating $C_2H_4(OH)_2$ and $C_2H_4Br_2$ to 160°, but the product boiled at 95°. Forms an iodide with 2 atoms of I, m.p. 84°, which is decomposed by water and air, but soluble in benzene ; also a sulphate and a picrate melting respectively at 100° and 66°. It also forms a compound with $HgCl_2$, soluble in, but slowly decomposed by, water (Faworsky, J. Russ. Phys. Chem. Soc. 38, 741 ; Paternò and Spallino, Atti. R. Acad. Lincei, [v.] 16, i. 87).

Chlorethylene oxide C_2H_3ClO ; b.p. 70°-80°. By long contact of acetylene chloriodide $CHCl : CHI$ with 40-50 vols. of water at 200°-220° (Sabanejeff, Annalen, 216, 268) ; difficultly soluble in water.

Bromethylene oxide $C_2H_3Br·O$; b.p. 80°-92°. From bromoglycol bromhydrin $CHBr_2·CH_2OH$ and KOH (Demole, Ber. 9, 51) ; soluble in water.

Ethylene phosphides r. PHOSPHORUS, ORGANIC COMPOUNDS OF.

Ethylene selenocyanate $C_2H_4(SeCN)_2$; m.p. 128° (Proskauer), 138° (Hagelberg, Ber. 23, 1092). From $CH_2Br·CH_2Br$ and alcoholic KCNSe (Proskauer, *ibid.* 7, 1281). Colourless needles, insoluble in cold water or ether, difficultly soluble in hot water or cold alcohol ; dissolves unchanged in strong HNO_3, but on heating gives ethylene selenious acid $C_2H_4(SeO_3H)_2$. With alcoholic alkali, yields ethylene diselenide (Hagelberg).

Diethylene disulphide $S\begin{matrix} CH_2·CH_2 \\ \diagup \quad\quad \diagdown \\ CH_2·CH_2 \end{matrix}S$; m.p. 111°-112° ; b.p. 199°-200° ; V.D.=4·28 (Husemann, Annalen, 126, 280). From $C_2H_4Br_2$ and K_2S (Crafts, *ibid.* 124, 110 ; 128, 220) ; also by heating $C_2H_4CS_2$ or $C_2H_4S_2Hg$ with $C_2H_4Br_2$ at 150° (H.).

Crystallises from alcohol in needles or leaflets, from ether in thick prisms which are volatile at ordinary temperatures ; combines with Br and certain salts, but not with NH_3 ; oxidised by HNO_3 to $(C_2H_4)_2S_2O_2$. The bromide

$$(C_2H_4)_2S_2Br_4$$

is a lemon-yellow amorphous body, m.p. 96°, very unstable ; the iodide $(C_2H_4)_2S_2I_4$, m.p. 132°-133°, forms iron-black monoclinic needles, insoluble in water. The oxide $(C_2H_4)_2S_2O_3$ can also be obtained by decomposition of the chloride or bromide ; with water, forms crystals which decompose without fusion on heating, and are soluble in water, almost insoluble in alcohol. The peroxide $(C_2H_4)_2S_2O_4$, obtained by heating $(C_2H_4)_2S_2$ with fuming HNO_3 to 150° (Crafts, Annalen, 124, 124), crystallises from strong HNO_3 in small crystals which are insoluble in water.

Ethylene ethylidene disulphide is obtained by heating ethylene sulphide almost to dull redness in absence of air and in a current of hydrogen sulphide. After being shaken with aqueous alkali is obtained as an almost colourless liquid, b.p. 172-173° (O. Matter, D. R. P. 313650).

Ethylene hydroxysulphide $C_2H_4(OH)SH$ (*Thioethylene glycol*), from $HO·CH_2CH_2Cl$ and alcoholic KHS ; the KCl is filtered off and the filtrate acidified with dilute HCl and evaporated at 30°-40° (Carius, Annalen, 124, 258). Is a heavy liquid, almost insoluble in water, soluble in alcohol ; the salts are fairly soluble in alcohol ; the mercury compound $Hg(C_2H_5OS)_2$ crystallises from alcohol in needles.

Thiodiethylene glycol $(C_2H_4OH)_2S$ is formed when the above compound is heated, H_2S being evolved. It is a crystalline solid ; m.p. under 60°, soluble in alcohol, insoluble in water, forms salts and double compounds with metallic salts.

Ethylene mercaptan $C_2H_4(HS)_2$; b.p. 146° ; sp.gr. 1·123 at 23·5°. From $CH_2Cl·CH_2Cl$ (or bromide, Werner, J. 1862, 424) and alcoholic KHS (Löwig and Weidmann, Annalen, 36, 322). A colourless liquid, soluble in alcohol and alkalis, forms insoluble mercaptides with heavy metals ; $Pb(C_2H_4)_2S_2$ yellow ; $Cu(C_2H_4)_2S_2$ chrome green. *Ethylene dimethyl sulphide* $C_2H_4(SCH_3)_2$, b.p. 183°, from $C_2H_4Br_2$ and CH_3SNa (Ewerlöf, Ber. 4, 716). *Ethylene*

diethyl sulphide $C_2H_4(SC_2H_5)_2$, b.p. 210°-213° (E.) gives on oxidation first $(C_2H_5SO)_2C_2H_4$, m.p. 170°; and next $(C_2H_5SO_2)_2C_2H_4$, m.p. 136·5° (Beckmann, J. pr. Chem. [2] 17, 469).

Ethylene thiocarbonates.

1. *Ethylene dithiocarbonate* $C_2H_4COS_2$, *ethylene oxythiocarbonate*; m.p. 31°; by action of HNO_3 upon $C_2H_4CS_3$ in the cold (Husemann, Annalen, 126, 269); forms long thin tables, insoluble in water, soluble in alcohol, ether, and chloroform.

2. *Ethylene trithiocarbonate* $C_2H_4CS_3$; m.p. 39·5° (Husemann), 33·4° (Konowalow), 39° (Frasetti); sp.gr. 1·4768. From $C_2H_4Br_2$ and Na_2CS_3 in presence of absolute alcohol (Husemann, Annalen, 123, 83); by action of water upon $AlBr_3·C_2H_4Br_2·CS_2$ (Konowalow); by action of alcoholic KOH upon ethylene xanthate

$$C_2H_4(S·CS·OEt)_2 + KOH$$
$$= KS·CO·OEt + C_2H_4CS_3 + EtOH$$
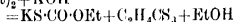
a theoretical yield; it reacts with dil. KOH thus:

$$C_2H_4CS_3 + EtOH + 3KOH$$
$$= KS·CO·OEt + C_2H_4S_2K_2 + 2H_2O$$
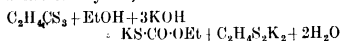
(Frasetti, Ber. 38, 488). Forms golden-yellow, rhombic prisms; slowly soluble in alcohol, easily soluble in ether, very soluble in CS_2, $CHCl_3$, and C_6H_6.

$\beta\beta'$-**Dichloroethyl sulphide** $(CH_2Cl·CH_2)_2S$, so-called 'mustard gas,' was apparently obtained by Guthrie (Chem. Soc. Trans. 1860, 12, 116; 1861, 13, 35) and by A. Niemann (Ann. 1860, 113, 288) by passing ethylene into cooled sulphur dichloride:

$$2CH_2 : CH_2 + SCl_2 = (CH_2Cl·CH_2)_2S$$
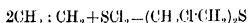
The conditions for its formation by this reaction have been studied by Myers and Stephen (J. Soc. Chem. Ind. 1920, 39, 65, T), and by Gibson and Pope (Chem. Soc. Trans. 1920, 117, 272). May also be prepared by converting ethylene into ethylene chlorohydrin, thence into thiodiglycol by treatment with sodium sulphide, and thiodiglycol into $\beta\beta'$-dichloroethyl sulphide by the action of hydrogen chloride:

(1) $CH_2 : CH_2 + HClO = CH_2Cl·CH_2·OH$

(2) $2CH_2Cl·CH_2·OH + Na_2S$
$$= (HO·CH_2·CH_2)_2S + NaCl$$

(3) $(HO·CH_2·CH_2)_2S + 2HCl$
$$= (CH_2Cl·CH_2)_2S + 2H_2O$$
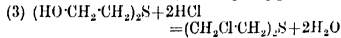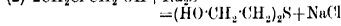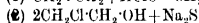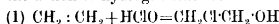
(V. Meyer, Ber. 1886, 19, 3260; Clarke, Chem. Soc. Trans. 1912, 101, 1583). For the conversion of ethylene chlorohydrin into dichloroethyl sulphide, *see* Gomberg, J. Amer. Chem. Soc. 1919, 41, 1414.

$\beta\beta'$-Dichloroethyl sulphide is more readily procured by the action of ethylene on sulphur monochloride at about 60°

$$2CH_2 : CH_2 + S_2Cl_2 = (CH_2Cl·CH_2)_2S + S$$

The product has either the constitution

$$(C·H_2Cl·CH_2)_2S : S$$
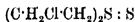
or is a colloidal solution of S in $(C_2H_4Cl)_2S$. According to Gibson and Pope, Guthrie's compound is a disulphide of the constitution

$$CH_2Cl·CH_2·S·S·CH_2·CH_2Cl$$
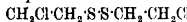
(Guthrie, l.c.; Gibson and Pope, l.c.; cf. J. Soc. Chem. Ind. 1919, 38, 348, T, et seq.).

The conditions for its preparation on a technical scale by this reaction were worked out by A. G. Green.

A continuous vacuum still for its manufacture is described by Streeter (J. Ind. Eng. Chem. 1919, 11, 292).

$\beta\beta'$-Dichloroethyl sulphide, when pure, boils at 120°/34 mm., 122·5°/37 mm., and 217°/760 mm. and readily solidifies in cold weather, forming long, colourless needles or prisms, which melt at 13·5° to a liquid of sp.gr. 15°/4°=1·285. It is almost insoluble in water, and is readily hydrolysed by boiling with an alcoholic solution of soda. For other physical properties, *see* Gibson and Pope; for a number of synthetic reactions, *see* Davies (Chem. Soc. Trans. 1920, 117, 297). It causes intense inflammation and suppuration when in contact with the skin or when breathed. First used on account of its physiological and toxic action as an offensive agent by the Germans during an attack on Ypres in June, 1917.

For a method of quantitative estimation of the substance in air, *see* J. Amer. Chem. Soc. 1920, 42, 266.

The existence of the so-called *chloroethylene dithiodichloride* $(C_2H_4Cl)_2S_2Cl_2$ (?), said to be obtained by the action of C_2H_4 upon boiling S_2Cl_2, and described as a light yellow liquid with a pleasant smell, is doubtful.

On treating $\beta\beta'$-dichloroethyl sulphide with concentrated nitric acid it is converted into $\beta\beta'$-*dichloroethyl sulphoxide* $(CH_2Cl·CH_2)_2SO$, colourless plates, m.p. 51°, and afterwards the sulphone $(CH_2Cl·CH_2)_2SO_2$, m.p. 110° (Spica, Gazz. chim. ital. 1919, 49, ii. 299). Treated with bromine the dichloroethyl sulphide yields $(CH_2Cl·CH_2)_2S,2Br_2$, an orange-coloured substance which rapidly loses bromine, and is converted into a bright-yellow solid

$$(CH_2Cl·CH_2)_2S,Br_2$$
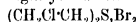
m.p. 43°-44° (Gibson and Pope).

Ethylenethiocyanate $C_2H_4(SCN)_2$; m.p. 90°. From $CH_2Cl·CH_2Cl$ and alcoholic KCNS (Sonnenschein, J. 1855, 609; Buff, Annalen, 100, 229); $CH_2Br·CH_2Br$ may be used with advantage (Glutz, *ibid.* 153, 313); forms rhombic plates slightly soluble in cold water, more so in hot, and in alcohol, decomposed by heat, volatile in steam; its vapour excites tears.

Ethylidene acetamide $CH_3CH(NHC_2H_3O)_2$; m.p. 169°; formed by acting on acetamide with aldehyde; forms large prisms decomposed by acids (Tawildarow, Ber. 5, 477).

Ethylidene acetate $CH_3·CH(C_2H_3O_2)_2$; o.p. 169°; sp.gr. 1·061 at 12°. From aldehyde and $(C_2H_3O)_2O$ at 180° (Geuther, Annalen, 106, 249); from alcoholic $C_2H_3O_2K$ and $CH_3CHCl·C_2H_3O_2$ (Schiff, Ber. 9, 304); by passing acetylene into a solution of mercuric oxide in glacial acetic acid to which an alkyl sulphate, particularly methylene sulphate, has also been added (Eng. Pat. 112766, 1918); or β-naphthalene sulphonic acid dissolved in glacial acetic acid may be used instead (Eng. Pat. 112765); has a smell like that of onions, and is decomposed by water into aldehyde and acetic acid.

Ethylidene azine $CH_3CH : N·N : CHCH_3$; b.p. 95°-96° at 760 mm.; sp.gr. 0·832 at 17°. Prepared by shaking an ethereal solution of aldehyde with an aqueous solution of hydrazine hydrate. At 180° it is unchanged, but at a higher tempera-

ture gives off nearly all its N as gas. It is fairly stable to alkalis, but is hydrolysed by acids into aldehyde and hydrazine (Curtius and Linkeisen, J. pr. Chem. 1898, [ii.] 58, 310).

Ethylidene biuret $NH<^{CO \cdot NH}_{CO \cdot NH}>CH \cdot CH_3$, *Trigenic acid*, by leading HCNO into well-cooled aldehyde (Liebig and Wöhler, Annalen, 59, 296), crystallises in small prisms, slightly soluble in water, nearly insoluble in alcohol, has a slightly acid taste. When heated, liberates CO_2, NH_3, and traces of collidine $C_8H_{11}N$ (Herzig, Monatsh. 2, 398). Is hardly decomposed by NaBrO. HNO_3 decomposes it and liberates cyanuric acid. The silver compound $AgC_4H_5N_3O_2$ forms amorphous precipitate, soluble in boiling water.

Ethylidene bromide $CH_3 \cdot CHBr_2$, b.p. 114°–115° (Tawildarow, *ibid.* 176, 12), 109°–110° at 751 mm. (Denzel, *ibid.* 195, 202), 110·5° at 760 mm. (Anschutz, *ibid.* 221, 137), 108°–110° (corr.) (Perkin, Chem. Soc Trans. 45, 523); b.p. 107°–108° (V. Meyer and Muller, J. pr. Chem. [2] 46, 168); sp.gr. 2·129 at 10° (T.), 2·1001 at 17·5°/4° 2·0891 at 20·5°/4° (Anschutz) 2·0822 at 21·5°/4°, 2·1029 at 15°, 2·0854 at 25° (P.). From C_2H_5Br and Br at 170° (Hofmann, Proc. Roy. Soc. 10, 619; Cawentou, Compt. rend. 52, 1330). Is produced by action of PCl_3Br_2 but not of PBr_5 upon aldehyde (Paternò and Pisati, Ber. 5, 289); also by heating $CH_3 \cdot CHBr$ with HBr to 100° (Reboul, Compt. rend. 70, 398). A heavy liquid; alcoholic KHS has no action upon it. On heating with water and PbO to 130°, aldehyde and HBr are produced (T.). With $SbCl_5$ gives $CH_3 \cdot CHCl_2$ (Henry, Bull. Soc. chim. [ii.] 42, 262).

Ethylidene bromiodide CH_3CHBrI; m.p. below $-20°$; b.p. 142°–143°; sp.gr. 2·50 at 1°, 2·452 at 16°. From C_2H_3Br and HI in the cold (Pfaundler, J. 1865, 483; Reboul, Annalen, 155, 212); by shaking CH_3CHI_2 with 1Br solution (Simpson, Bull. Soc. chim. [ii.] 31, 412); decomposed by alcoholic KOH or Ag_2O into HI and C_2H_3Br; Br yields CH_3CHBr_2.

Ethylidene chlorobromide $CH_3 \cdot CHClBr$; m.p. 16·6° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 157); b.p. 84°–84·5° at 750 mm., 82·7° at 760 mm. (Stadel, Ber. 15, 2563); sp.gr. 1·667 at 16°. From C_2H_4Br and concentrated HCl at 100° (Reboul, Annalen, 155, 215); from C_2H_5Cl and Br in sunlight (Denzel, *ibid.* 195, 193). By action of Cl upon C_2H_5Br (Lescœur, Bull. Soc. chim. [ii.] 29, 483). Is decomposed at ordinary temperature by alcoholic KOH on long standing; with Ag_2O gives aldehyde; and with $AgC_2H_3O_2$ forms $CH_3CH(C_2H_3O_2)_2$ (L.).

Ethylidene chloriodide $CH_3 \cdot CHClI$; b.p. 117°–119°; sp.gr. 2·054 at 19°. By agitating a mixture of CH_3CHI_2 and ICl; formed also from CH_3CHCl_2 and AlI_3 (Simpson, Bull. Soc. chim. [ii.] 31, 411).

Ethylidene or Ethidene chloride $CH_3 \cdot CHCl_2$, m.p. $-101·5°$ (Schneider, Zeitsch. physikal. Chem. 22, 233), b.p. 57·4°–57·6° at 750·9 mm., sp.gr. 1·1743 at 20°/4° (Brühl, Annalen, 203, 11), 1·2124 at 0°, 1·1805 at 22°/0°; refractive index μ_A (at 24·7°) = 1·405724. R_α = 34·1 (Kanonnikow); b.p. 57°–57·7° at 738·7 mm., 2·2013 at 0° (Pribram and Handl, Monatsh. 2, 659); b.p. 56·7°–56·9° at 749·1 mm., sp.gr. 1·1895 at 9·8°/4°, 1·11425 at 56·7°/4° (R. Schiff, Annalen, 220, 96), 57·32° (corr.) (Thorpe

and Rodger); crit. temp. 254·5° (Pawlewsky, Ber. 16, 2633); H.C.p. = 267·1 cals. (Berthelot and Ogier, Bull. Soc. chim. [ii.] 36, 68). From C_2H_5Cl and Cl (Regnault, Annalen, 33, 312); from C_2H_4O and PCl_5 (Beilstein). By action of HCl upon copper acetylene (Sabancjeff, *ibid.* 178, 111). Is prepared by passing a mixture of chlorine and C_2H_5Cl over animal charcoal heated to 250°–400° (Damoiseau, Bull. Soc. chim. [ii.] 27, 113). Is obtained as a by-product in the manufacture of chloral. Is decomposed by alcoholic KOH into HCl and C_2H_3Cl. Sodium produces · at 180°–200° hydrogen, acetylene, ethylene, ethane, and C_2H_3Cl (Tollens, Annalen, 137, 311). By action of Cl, CH_3CCl_3 and $CH_3Cl \cdot CHCl_2$ are produced.

Ethylidene di-*iso*-nitramine is formed by the interaction of $CO(Et)_2$, or $COEtMe$, and NO, in C_2H_5ONa. The lead salt is anhydrous and crystallises in cubes. The dimethyl ether forms rhombic crystals, and melts at 75°. The *iso*-nitramine itself is hydrolysed by mineral acids into acetaldehyde NH_2OH and oxides of N. With Na amalgam, is reduced to hydrazine (Traube, Annalen, 300, 120).

Ethylidene diethyl ether
$$CH_3 \cdot CH(OC_2H_5)_2 \; (v. \; \text{ACETAL}).$$

Ethylidene dimethyl ether $CH_3CH(OCH_3)_2$, *Dimethyl acetal*; b.p. 64·4° (Dancer, Annalen, 132, 240), 62·7°–63·3° at 757·6 mm. (R. Schiff, *ibid.* 220, 104); sp.gr. 0·8787 at 0°, 0·8590 at 14°, 0·8476 at 25° (D.), 0·8013 at 62·7°/4° (S.); capillarity constant at b.p. $a^2 = 4·092$ (Schiff, Annalen, 223, 74); occurs in crude wood spirit (D.): 2 volumes of wood spirit, 1 volume aldehyde, and ½ volume of glacial acetic acid are heated to 100° (Alsberg, J. 1864, 485); also by oxidation of CH_3OH and C_2H_5OH by MnO_2 and H_2SO_4 (Wurtz).

Ethylidene methyl propyl ether
$$CH_3 \cdot CH(OCH_3)(OC_3H_7)$$
b.p. 103°–105° (Bachmann, Annalen, 218, 46).

Ethylidene ethyl propyl ether
$$CH_3 \cdot CH(OC_2H_5)(OC_3H_7)$$
b.p. 124°–126° (Bachmann, *l.c.*).

Ethylidene dipropyl ether $CH_3 \cdot CH(OC_3H_7)_2$; b.p. 146°–148°, sp.gr. 0·825 at 22° (Girard, J. 1880, 695).

Ethylidene methyl *iso*butyl ether
$$CH_3 \cdot CH(OCH_3)(OC_4H_9)$$
b.p. 125°–127° (Claus and Trainer, Ber. 19, 3005; Bachmann, *l.c.*).

Ethylidene ethyl *iso*butyl ether
$$CH_3 \cdot CH(OC_2H_5)(OC_4H_9)$$
b.p. 155° (Claus and Trainer, *l.c.*).

Ethylidene di *iso*butyl ether $CH_3 \cdot CH(OC_4H_9)_2$; b.p. 168°–170°, sp.gr. 0·816 at 22° (Claus and Trainer, *l.c.*; Girard, *l.c.*).

Ethylidene methyl *iso*amyl ether
$$CH_3 \cdot CH(OCH_3)(OC_5H_{11})$$
b.p. 141°–144° (Bachmann, *l.c.*).

Ethylidene ethyl *iso*amyl ether
$$CH_3 \cdot CH(OC_2H_5)(OC_5H_{11})$$
b.p. 165°–167° (Claus and Trainer, *l.c.*).

Ethylidene di isoamyl ether $CH_3CH(OC_5H_{11})_2$
b.p. 210·8° (corr.), sp.gr. 0·8347 at 15° (Claus and Trainer, *l.c.*).

Ethylidene hydramine $CH_3 \cdot CH(OH)NH_2$ v. *Aldehyde-ammonia*, art. ALDEHYDE.

Ethylidene imine $CH_2CH:NH$; m.p. about 85° ; b.p. 123°–124°. If aldehyde ammonia be kept *in vacuo* over H_2SO_4 for several days, the imine is formed. It crystallises in brilliant colourless crystals, which have an odour like acetamide. It is soluble in water, EtOH, CH_3COOH, $CHCl_3$, C_6H_6, and toluene. The vapour density at 260° agrees with the simple formula, but at lower temperatures the V.D. is higher. It forms a picrate, and combines with HCN to form $CH_3 \cdot CH(NH_2)CN$. It polymerises to form trimeric ethylidine imine

$$CHMe \overset{NH \cdot CHMe}{\underset{NH \cdot CHMe}{\overbrace{\hspace{1.5cm}}}} NH$$
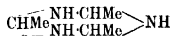
which forms a trinitroso- derivative, with N_2O_3 in $CHCl_3$; opaque yellow-white needles, melting at 161° (Delépine, Compt. rend. 1897, 125, 951 ; and 1907, 144, 853).

Ethylidene iodide CH_3CHI_2 ; b.p. 177°–179° ; sp.gr. 2·84 at 0°. By combination of C_2H_2 and HI (Berthelot, Annalen, 132, 122 ; Semenow, Zeitsch. Chem. 1865, 725) ; from CH_3CHCl_2 and Al_2I_6 (Gustavson, J. Russ. Phys. Chem. Soc. 6, 164) ; from C_2H_5Br and HI (Friedel, Ber. 7, 823). Decomposed by alcoholic KOH into HI and C_2H_3I.

Ethylidene malonic acid $CH_3 \cdot CH:C(COOH)_2$; only known in combination, the *ethyl ester* $CH_3CH:C(COOC_2H_5)_2$, b.p. 220°, 115°–118° at 17 mm. ; sp.gr. 1·0435 at 15°. From $CH_2(CO_2Et)_2$ (1 mol.) aldehyde (2 mols.), and $(C_2H_3O)_2O$ (1½ mols.) at 100° (Komnenos, Annalen, 218, 157). An ethereal oil smelling of camphor ; by long contact with $Ba(OH)_2$ in the cold yields ethoxy malonic acid $C_5H_8O_5$, malonic acid $C_3H_4O_4$, and aldehyde.

Ethylidene oxide $CH_3 \cdot CHO$ v. ALDEHYDE.

Ethylidene ethylene oxide

$$CH_3 \cdot CH \overset{OCH_2}{\underset{OCH_2}{\big\langle}}$$
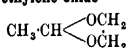
b.p. 82° (Verley, Bull. Soc. chim. [iii.] 21, 276), 82·5° at 765·8 mm. ; sp.gr. 1·002 at 0°. From aldehyde and excess of glycol at 100° (Wurtz, Compt. rend. 53, 378 ; Annalen, 120, 328) ; a liquid with irritating smell, soluble in 1½ vols. water, from which $CaCl_2$ separates it ; with acetic acid gives glycol diacetate.

Ethylidene ethoxyacetate $CH_3CH(OEt)OAc$; b.p. 125°–130° ; sp.gr. 0·941. By heating together acetal and acetic anhydride for 3 hours at 150°. A pleasant-smelling oil, slowly decomposed by cold water into alcohol, aldehyde, and acetic acid, rapidly on boiling.

Ethylidene sulphonic acids.

1. *Ethylidene hydroxysulphonic acid*

$$CH_3CH(OH)(HSO_3)$$
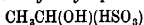
Salts of this acid are formed by action of aldehyde upon alkaline hydrogen sulphites ; they are crystalline bodies, soluble in water, and decomposed on heating into water, aldehyde, and sulphites.

2. *Ethylidene chlorsulphonic acid*

$$CH_3 \cdot CH \cdot Cl(SO_3H)$$
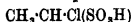
obtained by action of CH_3CHCl_2 upon neutral alkaline sulphites at 140° ; the salts are crystalline, and the acid is fairly stable.

3. *Ethylidene disulphonic acid*

$$CH_3CH(SO_3H)_2$$
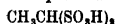
By oxidation of trithioaldehyde $(C_6H_6S_3)$ or thialdin by $KMnO_4$ solution (Guareschi, Gazz. chim. ital. 9, 75 ; Annalen, 222, 302). 10 grams thialdin are treated with 30–35 grams $ZnMn_2O_8$ and 300 grams water ; after filtering, BaH_2O_2 is added and excess of Ba precipitated by CO_2 ; the Ba salt is then precipitated by alcohol. It forms a strongly acid oily liquid, very soluble in water and alcohol, and is very stable ; forms stable salts $Na_2C_2H_4S_2O_6,H_2O$, small silky crystals soluble in 6071 parts of alcohol (90 p.c.) at 24·5° ; $K_2C_2H_4S_2O_6,2H_2O$ forms large transparent crystals soluble in 1·56 parts of water at 17°.

ETHYL ACETATE v. *Alkyl acetates*, art. ACETIC ACID.

ETHYL-m-AMINOPHENOL
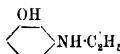
(1) Prepared by adding monoethyl aniline to fuming sulphuric acid, converting the ethyl aniline-m-sulphonic acid into the sodium salt, melting this with potassium hydroxide at 220°, dissolving the product in water, and acidifying with hydrochloric acid. The filtered solution is neutralised with sodium carbonate, and the mono ethyl-m-amino phenol extracted with benzene (Bad. Anil. und Soda Fabrik. D. R. P. 48151).

(2) Sodium-m-phenylene oxamate

$$C_6H_4(NH \cdot CO \cdot CO_2Na)$$
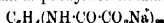
is mixed with sodium ethyl sulphate, alcohol, and sodium carbonate, and heated in an autoclave fitted with a stirrer to 180°. After distilling off the alcohol, and extracting the mass with water, the residue is boiled with dilute sulphuric acid, and the cooled solution of ethyl-m-phenylenediamine sulphate is mixed with sodium nitrite, warmed, and neutralised with sodium carbonate (*idem.* D. R. P. 76419).

(3) Aniline-2 : 5-disulphonic acid is neutralised with alkali, and the solution diluted, mixed with sodium ethyl sulphate, and heated in an autoclave to 170°–180°. Sodium carbonate is added to the cooled solution which precipitates ethyl-m-aminophenol (Farberfabrik. vorm. F. Bayer & Co., D R. P. 82765) ; m.p. 62° ; b.p. 176°/12 mm.

ETHYLANILINE
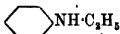
Is manufactured by heating aniline hydrochloride with alcohol in an autoclave at 180°. The hydrochloride separates out on cooling. Or aniline hydrochloride may be boiled with diethylaniline under a reflux condenser, hydrochloric acid added, and the hydrochloride separated by crystallisation. The base boils at 206°/760 mm. ; sp.gr. 0·954 at 18°. Yields methyl ethyl aniline on methylation, and benzyl ethyl aniline on benzylation.

ETHYLBUTYLACETIC ACID v. OCTOIC ACIDS.

ETHYL-iso-BUTYLACETIC ACID v. OCTOIC ACIDS.

ETHYL BUTYRATE v. BUTYRIC ACID.

ETHYL DIPHENYLAMINE v. DIPHENYLAMINE.
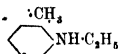
ETHYLKETENE v. KETENES.

ETHYLKETENECARBOXYLATE v. KETENES.

ETHYLMALONIC ACID v. GLUTARIC ACID and MALONIC ACID.

ETHYLMORPHINE v. OPIUM.

**ETHYLPROPYLACETIC ACID** v. HEPTOIC ACIDS.

ETHYL-o-TOLUIDINE

.⋅CH₃

NH⋅C₂H₅

May be prepared by heating a mixture of o-toluidine, ethyl alcohol, and hydrochloric acid, or a mixture of o-toluidine, ethyl alcohol, and a small quantity of iodine. Boils at 213°–214°; sp.gr. 0·9534.

EUBORNYL. Trade name for bornyl-α-bromo-isovalerate, obtained by brominating chloro-isovaleric acid and esterifying borneol with the product.⋅ A syrupy aromatic liquid; b.p. 175°–178°. Used as a sedative (v. SYNTHETIC DRUGS).

α-EUCAINE. Methyl ester of N-methyl-benzoyl-triacetone-alkamine carboxylic acid. First obtained by Merling (Ber. Deut. pharm. Ges. 1897, 173) by acting on acetone with ammonia to form triacetoneamine, treating this with hydrocyanic acid to form the cyanhydrin,
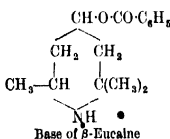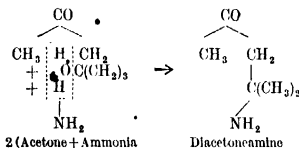
which by hydrolysis yields triacetone-alkamine-carboxylic acid. On benzoylation and methylation it forms α-eucaine. Formerly employed as a substitute for cocaine. Its use is now superseded by β-eucaine, which is less painful and not so toxic.

β-EUCAINE (benzoyl-vinyl-diacetone-alkamine)

CH—O⋅CO⋅C₆H₅

H₂C   CH₂

(CH₃)₂C   CH⋅CH₂

NH
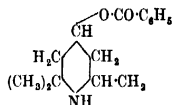
A local anæsthetic, used chiefly as the lactate or hydrochloride, in 2–3 p.c. solution. Is prepared by condensing acetone with oxalic acid and ammonia to form the hydrogen oxalate of diacetoneamine, condensing this with paraldehyde to produce the cyclic vinyl-diacetoneamine (Harries, Annalen, 1897, 328; 1898, 346), reducing by means of sodium amalgam to a mixture of the cis and trans forms of the trimethyl hydroxy piperidine (D. R. P. 95622), treating with sodium amylate to produce the cis form only of this compound (D. R. P. 95621), and treating with benzoyl chloride (D. R. P. 97672), and finally with hydrochloric or lactic acid to obtain the corresponding salt of β-eucaine.

2 (Acetone + Ammonia) → Diacetoneamine → Vinyl-diacetoneamine ↓ Reduction → Vinyl-diacetone-alkamine

Base of β-Eucaine
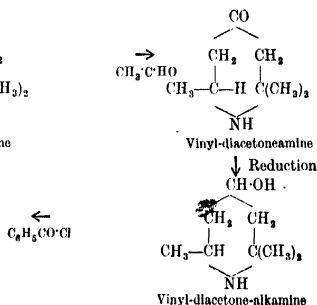
EUCAINE, EUCHININ, EUCODIN, EUCOL, EUDOXIN v. SYNTHETIC DRUGS.

EUCAIRITE. Selenide of silver and copper (Ag,Cu)₂Se, crystallising in the cubic system. It is lead-grey, but usually tarnished and dull; sp.gr. 7·5. It is found massive and granular embedded in calcite in the Skrikerum copper mine in Småland, Sweden, and in the Cacheuta mine in the province of Mendoza, Argentina.

L. J. S.

EUCALYPTOL. The volatile oil of the leaves of *Eucalyptus globulus*, consists mainly of a body C₁₀H₁₈O; b.p. 176°–177°; sp.gr. 0·923 at 16°. It is optically inactive, has a camphor-like smell, and is probably identical with cineol and cajeputol (v. OILS, ESSENTIAL).

EUCALYPTUS GUM v. KINO.

EUCALYPTUS MACRORHYNCHA. *Eucalyptus macrorhyncha* (F. v. M.), a fair-sized tree, is the 'red stringy bark' of New South Wales,

and the ordinary stringy bark tree of Victoria (Smith, Chem. Soc. Trans. 1898, 73, 697).

The leaves yield under favourable conditions a very large amount (10 p.c.) of a crystalline glucoside termed by Smith *myrticolorin*, which can be isolated in the crude condition by mere extraction with boiling water. The solution on cooling became semi-solid owing to the separation of crystals, and these can be purified by extraction with ether to remove chlorophyll and crystallisation first from alcohol and subsequently from water. It formed pale-yellow needles, gave on hydrolysis quercetin and glucose, and at first appeared to be a new glucoside of quercetin. Though very similar to rutin its identity with this glucoside was unsuspected in that rutin by hydrolysis was presumed at that time to give quercetin and 2 molecules of rhamnose (Schunck, ibid. 1888, 53, 264). Schmidt in 1908 (Arch. Pharm. 246,

214), however, pointed out that rutin in this manner yields not only rhamnose but glucose, and the probability that myrticolorin—as also viola quercitrin and osyritrin—were identical with rutin was subsequently confirmed by Perkin (*ibid.* 1910, 97, 1776). A. G. P.

EUCALYPTUS OIL *v.* OILS, ESSENTIAL.

EUCALPYTUS RESIN *v.* RESINS.

EUCLASE. Basic silicate of aluminium and glucinum (GlO, 17·3 p.c.) HGlAlSiO₅, crystallising in the monoclinic system. The well-developed crystals have a very perfect cleavage parallel to the plane of symmetry, hence the name, from εὖ, well, and κλάσις, fracture. They are colourless, yellow, green, or blue ; sp.gr. 3·1 (higher than that of beryl) ; H. 7½. The mineral is not attacked by acids, and the water is expelled only at a high temperature. It is found as single isolated crystals in gold washings at Ouro Preto in Brazil, and on the River Sanarka in the southern Urals. Minute crystals have also been found in mica-schist in the Grossglockner district of the Austrian Alps, and in granite in the Fichtelgebirge, Bavaria. The mineral is occasionally cut as a gem-stone, but it has the drawback that it readily splits along the perfect cleavage. L. J. S.

EUCODAL. Trade name for the hydrochloride of dihydrohydroxycodemone. Used as a narcotic.

EUCODEINE. Syn. for codeine methyl bromide.

EUCOL. Trade name for guaicol acetate.

EUCOLITE *v.* EUDIALYTE

EUCRYPTITE. Orthosilicate of aluminium and lithium (Li₂O, 11·9 p.c.) LiAlSiO₄, crystallising in the hexagonal system and belonging to the nephelite group of minerals. It occurs intimately intergrown with albite as an alteration product of spodumene at Branchville, Connecticut. An artificial orthorhombic form of LiAlSiO₄, dimorphous with eucryptite, has been called *pseudo-* or *β-eucryptite* (F. M. Jager and A. Simek, 1914). L. J. S.

EUCUPIN. Trade name for *iso*-amylhydrocuprein.

EUDESMIN C₂₂H₂₆O₆ occurs in the kinos of eucalyptus species, the oils of which contain cineole and pinene, but not phellandrene. It may be obtained by extracting a concentrated aqueous solution of the kino with ether, purifying by treatment with chloroform, and crystallising from methyl alcohol. Colourless prismatic needles, m.p. 107°, $[a]_D^{21}$ −64·1° (in chloroform). Contains 4 methoxy- groups, and is unacted upon by hydroxyl or ketone reagents. Red solution with sulphuric acid. Nitric acid converts it into *dinitroeudesmin*, colourless needles, m.p. 214°. Boiling conc. nitric acid forms 4 : 5-dinitroveratrole (2 mols). Chlorine in acetic acid solution gives *dichloroeudesmin* ; colourless rectangular plates, m.p. 163°. *Dibromoeudesmin*, prepared in like manner, colourless needles, m.p. 172°, $[a]_D^{22}$ +69·4° (in chloroform) ; this, on oxidation with permanganate, gives 6-bromoveratric acid, m.p. 184°. *Diiodoeudesmin*, needles, m.p. 175° (Robinson and Smith, J. Roy. Soc. New South Wales, 1914, 48, 449).

EUDIALYTE. Silicate and zirconate (ZrO₂,

14–16 p.c.) of sodium, calcium, and ferrous iron, occurring as large well-developed rhombohedral crystals. These are brownish-red or rose-red in colour ; sp.gr. 2·9–3·1. The mineral occurs in nepheline- and sodalite syenites in the Julianehaab district in south Greenland, at Magnet Cove in Arkansas, on Sedlovatoi Island in the White Sea, and on the Kola peninsula in Russian Lapland. The name eudialyte, from εὖ, well, and·διαλύειν, to dissolve, refers to the fact that the mineral is readily decomposed by acids.

Eucolite, a closely related variety, differs in being optically negative, instead of positive. This is from the nepheline-syenites of the Langesundsfjord in Norway. L. J. S.

EUDRENINE. A solution containing eucaine and adrenaline.

EUFORMOL. Dextrin formaldehyde.

EUGENOL $(HO)(CH_3O)C_6H_3·CH_2·CH : CH_2$ $(C_3H_5 : CH_3O : HO = 1 : 3 : 4)$ occurs in oil of cloves from the leaves of *Eugenia caryophyllata* (Thunb.) (Bonastre and Ettling, Annalen, 9, 68) ; in the oil from the leaves of the Ceylon cinnamon tree (Stenhouse, Annalen, 95, 103 ; Schimmel & Co., Chem. Zentr. 1902, ii. 1486) ; from *Cinnamomum pedatinervium* (Meissn.) (Goulding, Chem. Soc. Trans 1903, 1101), *C. Tamala* (Nees et Eberm.) (Schimmel & Co., Chem. Zentr. 1910, i. 1720), *C. cassia* (Blume), and *C. zeylanicum* (Nees) (Duyk, Chem. Zentr. 1896, ia. 358 ; Weber, Arch. Pharm. 230, 232) ; ·from the fruit of *Pimenta officinalis* (Lindl.) (Bonastre, *l.c.* ; Oeser, Annalen, 131, 277) ; from the sap of *Acacia Farnesiana* (Willd.) (Walbaum, J. pr. Chem. 68, [2] 235) ; in the oil from *Ocimum Basilicum* (Linn.) (Schimmel & Co., Chem. Zentr. 1900, i. 906) ; in calamus oil (Thoms and Beckstroem, Ber. 1902, 3187) ; in Ylang Ylang oil (Schimmel & Co., Chem. Zentr. 1903, i. 1087 ; ii. 272) : in olive oil from Pugh (Canzoneri, Gazz. chim. ital. 1897, 27, ii. 1) ; in oil of nutmeg (Power and Salway, Chem. Soc. Trans. 1907, 2041) ; in sassafras leaves and bark (Pomeranz, Monatsh. 11, 101 ; Power and Kleber, Chem. Zentr. 1897, ii. 42) ; in the oil from the leaves of the bay tree (Mittmann, Arch. Pharm. 27, [3] 539) ; in oil from Maltese oranges (Gildemeister and Stephan, Arch. Pharm. 235, 583), and in other ethereal oils The methyl ether of eugenol

$$(CH_3O)_2·C_6H_3·CH_2·CH : CH_2$$
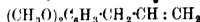
occurs in the oil of *Asarum canadense* (Linn.) (Power and Lees, Chem. Soc. Trans. 1902, 67), of *A. arifolium* (Michx.) (Miller, Arch. Pharm. 240, 371) ; in oil from Paracoto bark (Jobst and Hesse, Annalen, 199, 75 ;· Wallach and Rheindorff, *ibid.* 271, 300) ; in Ylang Ylang oil ; in oil from the bark of *Cinnamomum pedatinervium* ; in oil from Maltese oranges (*v. supra*) ; and in oil of citron (Schimmel & Co., Chem. Zentr. 1899, ii. 879).

Oil of cloves, which contains eugenol and a terpene as the chief constituents, is treated with potash ; the potassium salt of eugenol separates, is pressed out, washed with alcohol, and the eugenol set free by the addition of a mineral acid (Wasserman, Annalen, 179, 369). It is obtained by a similar process from oil of cinnamon leaves or from that of *Pimenta officinalis* (Lindl.). Another method consists in separating eugenol from oil of cloves by means of the compound it forms with sodium acetate (Chem.

Werke Byk D. R. P. 100418; Chem. Zentr.
1899, i. 764). In the former process, a residue
is left after treating the oil of cloves with
potash, and by distilling this under reduced
pressure, acetyl eugenol, m.p. 29°, is obtained
(Erdmann, J. pr. Chem. 1897, [2] 56, 146). By
reducing coniferin in alkaline solution with
sodium amalgam, eugenol is formed (Chiozza,
Chem. Zentr. 1888, 443). Methyl eugenol (allyl
guaiacol) has been prepared synthetically by
treating veratrol (dimethylcatechol) with allyl
iodide and zinc-dust (Moureau, Compt. rend.
121, 721).

Pure eugenol is a colourless oil; b.p. 244·5°
(Frankforter and Lando, J. Amer. Chem. Soc. 27,
641), 247·5° (Wassermann, Annalen, 179, 366),
253·5° (corr.) (Perkin, Chem. Soc. Trans. 1896,
1247); sp.gr. 1·0785 at 4°/4°, 1·0734 at 10°/10°,
1·0663 at 20°/20°; specific magnetic rotation,
2·1974; molecular magnetic rotation at 15°,
18·727 (Perkin, l.c.); dielectric constant, 6·0
(Mathews, J. Phys. Chem. 9, 641); μ_D 1·54437;
sp. heat, ·0·5024; mol. heat of combustion,
1304 cals. (F. & L. l.c.). Eugenol reddens
litmus, smells strongly of cloves, and has a
burning taste. It does not reduce Barreswil's
solution, but reduces ammoniacal silver solu-
tions on long standing. Eugenol may be
detected by the following reactions: (i.) ferric
chloride imparts a blue colour to its alcoholic
solution; (ii.) zinc chloride yields a transitory
pale-yellow colour; (iii.) sulphuric acid gives
first a brown colour, changing quickly to purple
and finally to wine-red; (iv.) Burgess (Analyst,
1900, 25, 265) makes use of a reagent prepared
by dissolving 10 grams of mercuric salt in 25 p.c.
sulphuric acid, and making the solution up to
100 c.c. with the latter. By shaking 2 c.c. of
eugenol with 5 c.c. of the reagent, and allowing
the solution to stand, a pale violet colour is
developed. (For estimation of eugenol in oil
of cloves, v. Verley and Bösling, Ber. 1901,
3359; Thoms, Chem. Zentr. 1903, 27, 954;
Arch. Pharm. 241, 592; Spurge, Pharm.
J. 1903, [4] 16, 701, 757; Schimmel & Co.,
Chem. Zentr. 1903, ii. 1124; Reich, Zeitsch.
Nahr. Genussm. 1909, 18, 401.)

Eugenol and its derivatives are readily con-
verted into the corresponding derivatives of
the isomeric isoeugenol (v. infra), which on
oxidation yields vanillin and its derivatives.
Chromic acid oxidises eugenol to acetic acid,
carbon dioxide, and water (Wassermann, l.c.);
chromyl chloride, however, combines with
eugenol, and on decomposing the product with
water, vanillin can be extracted (Novarine,
U.S. Pats. 365918, 365919; Ber. Ref. 1896,
812). Nitric acid oxidises eugenol to oxalic
acid and a resin, but in ethereal solution, 5-
nitro-eugenol is formed (v. infra). Ferric
chloride oxidises it to dehydroeugenol, m.p.
105°–106° (Cousin and Hérissey, Compt. rend.
1908, 146, 1413). Oxidised with potassium
permanganate, eugenol yields homovanillin,
vanillin, and vanillic acid (Erlenmeyer, Ber.
1876, 273). Hydrogenisation of either eugenol
or isoeugenol in the presence of platinum black,
yields dihydroeugenol (propylguaiacol), b.p.
246°–248° (Fournier, Bull. Soc. chim. [4] 7, 23).

5-Nitroeugenol is prepared by acting on
eugenol in ethereal solution with nitric acid.
It forms large triclinic crystals, m.p. 43°–44°

(Weselsky and Benedikt, Monatsh. 3, 388).
With tin and hydrochloric acid, it produces
aminochlorhydroeugenol hydrochloride; amino-
chlorhydroeugenol melts at 97°. Nitroeugenol,
heated with acetic anhydride and sodium acetate,
forms nitro-aceto-eugenol, m.p. 61°, which,
oxidised by potassium permanganate at 70°
(Tiemann, Ber. 1876, 418), yields nitrovanillic
acid $C_6H_2(COOH)(OCH_3)(OH)NO_2$, decom-
posing at 210° without melting.

Acyl and aryl derivatives of eugenol are
obtained by treating eugenol with acyl or aryl
anhydrides in the cold, in presence of some con-
densing agent such as sulphuric acid, zinc
chloride, pyridine, &c. The chlorides may be
substituted for the anhydrides (Merck, D. R. P.
103581, 109445; Chem. Zentr. 1899, ii. 927;
1900, ii. 407; Riedel, D. R. P. 189333; Chem.
Zentr. 1908, i. 185; Pond & Beers, J. Amer.
Chem. Soc. 19, 825). Acetyl eugenol, which
occurs in oil of cloves (Erdmann, J. pr. Chem.
1897, [2] 56, 146), melts at 29°, and boils at
281°–282° (752 mm.) (Freyss, Chem. Zentr.
1899, i. 835); benzyl eugenol has b.p. 235°,
and on heating with potash and subsequently
with potassium dichromate and sulphuric acid,
the benzyl ether of vanillin is obtained (Boeh-
ringer and Sons, D. R. P. 65937; Ber. Ref.
1893, 211). Eugenol carbonate, m.p. 93°–94°, is
obtained by passing phosgene gas into an alkaline
solution of eugenol; on treatment with ammonia,
the carbamate is formed (F. von Heyden Nachf.
D. R. P. 58129; Ber. Ref. 1892, 186); the car-
bonate can also be obtained from eugenol and
the diphenyl ester of carbonic acid (D. R. P.
99057; Chem. Zentr. 1898, ii. 1190). On
adding eugenol to a cooled mixture of pyridine
and chlorsulphonic acid in carbon disulphide,
potassium eugenyl sulphate, m.p. 203°, is ob-
tained; the latter is transformed by heating
with excess of potash into potassium isoeugenyl-
sulphate, m.p. 223°, which, on oxidation with
ozone, yields potassium vanillin sulphate
(Verley, Bull. Soc. chim. 1901, [3] 25, 46).

Eugenyl acetic acid

$$C_6H_3(CH_2 \cdot CH : CH_2)(OCH_3)(OCH_2 \cdot CO_2H)$$
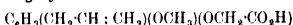
is obtained by heating eugenol with chloracetic
acid in the presence of sodium hydroxide for
20 hours, and decomposing the sodium salt thus
formed with hydrochloric acid; m.p. 75°. By
heating the acid with potash and amyl alcohol
at 150°, isoeugenyl acetic acid, m.p. 92°–94°, is
produced; and oxidation of the latter with
potassium permanganate yields vanillin acetic
acid (Bassmann and Krafft, Ber. 1895, 1870).

Eugenyl phosphoric acid is obtained by
treating eugenol with phosphorus oxychloride
and decomposing the resulting chloride with
water; m.p. of anhydrous acid, 105° (Boehringer
& Sons, D. R. P. 98522; Chem. Zentr. 1898,
ii. 950; Oeser, Annalen, 131, 277). On
heating with alcoholic potash, isoeugenyl
phosphoric acid is obtained, and by heating the
acid sodium salt of the latter to 150°, isoeugenol
is obtained quantitatively.

Eugenyl alcohol is prepared by heating
eugenol in 20 p.c. sodium hydroxide solution
with formaldehyde at 60°; m.p. 37°–38°
(Monasse, Ber. 1902, 3894).

Eugenol glucoside, m.p. 132°, is produced by
the action of acetochlorhydrose on the potassium

salt of eugenol (Michael, Amer. Chem. J. 6, 336).

Eugenol and isoeugenol form compounds with proteins which are stated to be used in the treatment of tuberculosis (Belart, Eng. Pat. 9246, 26075 ; Fr. Pat. 389889 ; J. Soc. Chem. Ind. 1908, 998 ; 1909, 1325).

(For compounds with iodine, v. F. v. Heyden Nachf. D. R. P. 70058 ; Ber. Ref. 1893, 915 ; Ingle, J. Soc. Chem. Ind. 1904, 422.) The N-substituted aminoethyl compounds of eugenol- and isoeugenol- acetamide are stated to be used as local anæsthetics (Einhorn, D. R. P. 208255 ; J. Soc. Chem. Ind. 1909, 491).

Bromine in excess forms with eugenol, di-bromeugenol dibromide, m.p. 118°-119°, which, treated with zinc-dust in alcoholic solution, yields dibromeugenol, m.p. 59° (Chasanowitz and Hell, Ber. 1885, 823 ; Auwers, ibid. 1901, 4266). By treating eugenol with bromine in chloroform at 0°, bromeugenol is formed (Lando, J. Amer. Chem. Soc. 1905, 27, 641). Tribrom-eugenol and other brom- derivatives (v. Lando, l.c. ; Auwers and Müller, Ber. 1902, 35, 114 ; Hell and Anwandter, ibid. 1895, 2085).

Eugenol methyl ether occurs in several ethereal oils, and can be obtained from veratrol (v. supra). It is also obtained by the action of methyl iodide and caustic potash on eugenol (Ciamician and Silber, Ber. 1890, 1164) ; b.p. 247°-248°. It is readily converted into iso-eugenol methyl ether, b.p. 263°, which yields methyl vanillin and veratric acid on oxidation with potassium dichromate and sulphuric acid.

isoEugenol

$(HO)(CH_3O) C_6H_3 \cdot CH:CH \cdot CH_3(C_3H_5:CH_3O:HO=1:3:4)$

occurs in small quantities in oil of nutmeg (Power and Salway, Chem. Soc. Trans. 1907, 2041), and as the methyl ether in the oil from Asarum arifolium (Michx.) (Miller, Arch. Pharm. 240, 371). It is prepared by adding 5 parts of eugenol or an equivalent quantity of oil of cloves to 12·5 parts of potash, dissolved in 18 parts of amyl alcohol, and heating for 16-20 hours at 140°. The product is steam distilled, and the residue acidified with sulphuric acid. The isoeugenol separates out, is washed with sodium carbonate solution, and purified by distillation (Tiemann, Ber. 1891, 2870 ; 1894, 2580 ; Lairi, Eng. Pat. 17547 ; J. Soc. Chem. Ind. 1891, 854 ; Haarmann and Reimer, D. R. P. 57808 ; Ber. Ref. 1892, 94). The amyl alcohol may be replaced by methyl, ethyl, or butyl alcohols (Gassmann, Compt. rend. 124, 38 ; F. von Heyden Nachf. D. R. P. 70274 ; J. Soc. Chem. Ind. 1892, 633). Other methods are to heat eugenol with 4 parts of caustic potash and some water at 220° (Einhorn and Frey, D. R. P. 76982 ; Frdl. iii. 863 ; Ber. 1894, 2455) ; to heat the alkali derivative of eugenol to 200° in the absence of air (Fritzsche, D. R. P. 179948 ; J. Soc. Chem. Ind. 1907, 1216) ; and to heat the acid sodium salt of iso-eugenylphosphoric acid to 150° (v. Eugenyl-phosphoric acid).

isoEugenol forms colourless crystals, m.p. 33°; b.p. 264°-265° (J. Soc. Chem. Ind. 1892, 633), 193·5° (100 mm.), and 266·5°-268·5° (760 mm.) ; sp.gr. 1·0994 at 4°/4°, 1·0944 at 10°/10°, 1·0872 at 20°/20° ; specific magnetic rotation ?·5578 ; molecular magnetic rotation at 15°, 21·469 (Perkin, Chem. Soc. Trans. 1896, 1247). On

oxidation, isoeugenol and its derivatives yield the corresponding derivatives of vanillin. Thus isoeugenol, when treated with sodium peroxide, yields vanillin itself (Haarmann and Reimer, Eng. Pat. 11952, 14925.; J. Soc. Chem. Ind. 1895, 506 ; 1897, 623 ; cf. Majert, D. R. P. 82924 ; Ber. Ref. 1895, 878). Ozone oxidises isoeugenol in the same way, and vanillin is also produced by the electrolysis of the sodium salt of isoeugenol and subsequent addition of acid (Otto and Varley, U.S. Pat. 553039, 553593 ; Ber. Ref. 1896, 249 ; cf. Otto, Ann. Chim. Phys. 1898, [viii.] 13, 120). Ferric chloride oxidises isoeugenol to dehydroisoeugenol, m.p. 133° (Cousin and Hérrisey, Compt. rend. 1908, 147, 247).

isoEugenol is readily polymerised by small quantities of mineral acids, acid chlorides, or metallic haloids, forming diisoeugenol, which crystallises in colourless needles, m.p. 178° (F. von Heyden Nachf. D. R. P. 70274 ; J. Soc. Chem. Ind. 1892, 633), 180° (Puxeddu, Gazz. chim. ital. 39, i. 131). Similarly, the ethyl ether of isoeugenol, when dissolved in alcohol and treated with hydrogen chloride for some hours, polymerises into diethyldiisoeugenol, m.p. 130° (Puxeddu, l.c. ; Wassermann, Annalen, 179, 375).

The acyl and aryl derivatives are obtained by methods similar to those employed for the eugenol compounds, but the solutions must be kept cool to prevent polymerisation taking place ; acetyl isoeugenol, m.p. 79°-80° ; benzoyl iso-eugenol, m.p. 103°-104° ; benzyl isoeugenol, m.p. 48° (Pond and Beers, J. Amer. Chem. Soc. 19, 825 ; Merck, D. R. P. 103581, 109445 ; Chem. Zentr. 1899, ii. 927 ; 1900, ii. 407 ; Haarmann and Reimer, D. R. P. 57568 ; Ber. Ref. 1892, 93). If acetyl chloride is added to isoeugenol at 54°, and the temperature is finally raised to 80°, diacetyldiisoeugenol is obtained, and by hydrolysis with acids, diisoeugenol is formed (Tiemann, Ber. 1891, 2870 ; 1894, 2580). Methylene chloride reacts with an alkaline solution of eugenol forming methylenediisoeugenol, m.p. 50°-52°, which on oxidation yields methyl-enedivanillin (Lesault & Co., D. R. PP. 75264, 76061 ; Ber. Ref. 1894, 812, 928).

5-Nitroisoeugenol is formed by the action of nitric acid on isoeugenol in acetic acid solution ; on recrystallisation from isobutyl or amyl alcohols it forms a reddish-yellow mass, which decomposes at about 150° (Puxeddu and Comella, Gazz. chim. ital. 1906, 36, ii. 450).

isoEugenol carbonate is prepared in the same way as eugenol carbonate (q.v.) (F. von Heyden Nachf. D. R. P. 61848 ; Ber. Ref. 1892, 486).

By adding excess of bromine to isoeugenol, bromisoeugenol dibromide, m.p. 138°-139°, is formed. If only 1 molecule of bromine is added, an unstable isoeugenol dibromide, m.p. 95°, is produced Di- and tri-isoeugenol dibromides have been prepared (Hell and Portman, Ber. 1895, 2088 ; Hell and Bauer, Ber. 1904, 1128 ; Zincke and Hahn, Annalen, 329, 1).

isoEugenol methyl ether occurs in the oil of Asarum arifolium (v. supra). It can be pre-pared by warming eugenol methyl ether with alcoholic potash (Ciamician and Silber, Ber. 1890, 1165) or by treating isoeugenol with dimethyl sulphate and aqueous potash (Mannich, Arch. Pharm. 248, 127) ; b.p. 263°.

*iso*Eugenol is distinguished from eugenol by the following reactions : (i.) ferric chloride gives an olive-green colouration with its alcoholic solution ; (ii.) zinc chloride, a bright rose-pink colour ; (iii.) sulphuric acid, a rose-pink colour changing to light-brown.

EUGUFORM, EUMYRDIN, EUPHTHAL-MIN, EUPORPHIN v. SYNTHETIC DRUGS.

EUKODAL. Oxydihydrocodeinone hydrochloride. Used as a narcotic (Freund and Speyer, Münch. med. Woch. 1917, 64, 380).

EULATIN. Trade name for a mixture of *p*-bromobenzoic acid, *o*-aminobenzoic acid, and antipyrine.

EUONYMUS (*Euonymi Cortex*, B.P.) (deleted from U.S. P. 1916) is the root bark of *E. atropurpureus* (Jaquin), a shrub indigenous to the United States, and known there as ' wahoo ' or ' burning bush.' It is said to contain an amorphous bitter principle and a glucoside *euonymin* : the latter, according to Hans Meyer (*cf.* Schmiedeberg, Arch. exp. Path. Pharm 1883, 16, 163), possesses a digitalis-like action, causing systolic arrest of the frog's heart in very small doses. Nothing is known about it chemically. For an account of earlier investigations, *v.* Rogerson (Chem. Soc. Trans. 1912, 101, 1040), who isolated dulcitol (2·1 p.c. of the bark) and other substances, but could not find any glucoside. The latter negative result may have been due to hydrolysis by the steam distillation employed. The name euonymin is also applied to dried extracts of varying composition, brown euonymin being from the root bark, and green (containing chlorophyll) from the stem bark.

<div align="right">G. B.</div>

EUPAD. An antiseptic consisting of equal weights of chloride of lime and boric acid.

EUPHORBIC ACID, EUPHORBIUM, EUPHORBONE v. GUM RESINS.

EUPHORINE v. SYNTHETIC DRUGS.

EUPHRASIA TANNIN v. TANNINS.

EUPHYLLIN. Trade name for a compound of theophylline with ethylene-diamine. A white crystalline soluble powder, used as a diuretic (*v.* SYNTHETIC DRUGS).

EUPITTONIC ACID, *Eupittone*, *Pittacal*, *Hexamethoxyaurin* $C_{25}H_{26}O_9$

$$O: \langle\!\!\!\!\!\bigcirc\!\!\!\!\!\rangle : C[C_6H_2(OMe)_2OH]_2$$
$$\overset{OMe}{\underset{OMe}{}}$$
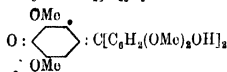
Pittacal is a blue colouring matter obtained by Reichenbach in 1835 from the high-boiling portions of beechwood tar. Grätzel also from the same products obtained a brown substance which gave the same blue colour reaction with baryta as the pittacal of Reichenbach. The colouring matter, which only exists in small quantity in this brown substance, was extracted and examined by Liebermann (Ber. 9, 334). It is an orange-red crystalline powder, soluble in alcohol and acetic acid, forming brown solutions. It forms with alkalis purple, and with ammonia blue solutions, from which carbon dioxide precipitates blue salts, soluble in pure water. Calcium, magnesium, barium, and tin salts also give blue precipitates with the alkaline solutions. The calcium and magnesium salts are soluble in water. Hydrochloric and sulphuric acids form red

solutions, and the latter turns pure blue on warming. In acid solutions, it dyes animal fibres orange, in ammoniacal solution especially with tin mordant, blue-violet. Liebermann called this colouring matter *eupittone*, and regarded it as at least closely allied to pittacal (Ber, 11, 1145). Hofmann (Ber. 12, 1371, 2216), by the action of hexachlorethane C_2Cl_6 on dimethyl pyrogallate mixed with alcoholic potash or soda, obtained a substance identical in composition with the eupittone of Liebermann, and strongly resembling it in properties. It is an orange-yellow substance, soluble in acetic acid, and precipitated therefrom by alcohol. It melts at 200° and decomposes partly into a blue sublimate. It forms the same alkali salts and gives the same sulphuric acid reaction as eupittone. This body is hexamethoxy-rosolic acid $C_{19}H_9(OC_2H_3)_6O_3$. Heated with alcoholic ammonia, it yields hexamethoxy-rosaniline

$$OH\cdot C[C_6H_2(NH_2)(OMe)_2]_3$$
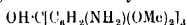
which crystallises in broad colourless needles, and has no tinctorial properties. When 2 grams eupittone are heated with 20 c.c. alcoholic methylamine (10 p.c.) at 150°–160° for 2½ hours, it yields hexamethoxydimethylformyl-*paraleucaniline*

$$CH[C_6H_2(OMe)_2NH\cdot CH_3]_2C_6H_2(OMe)_2NHCHO$$

m p. 187° (Liebermann, Ber. 34, 1034). Pyrogallol is produced in attempting to replace the methoxyl groups by hydrogen. Its formation is analogous to that of rosolic acid

$$3C_6H_{10}O_4 + CO_2 - C_{25}H_{26}O_9 + 2H_2O$$
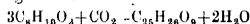
Hofmann terms thus body *eupittonic acid*, and uses the name as synonymous with pittacal and eupittone. Eupittone acid cannot be obtained by heating the sodium derivative of dimethyl pyrogallate or of dimethyl-methyl-pyrogallate separately, in air ; a mixture of the two, however, with excess of soda gives sometimes as much as 10 p.c. of its own weight of the acid. The action is comparable with that in which rosaniline is produced from aniline and toluidine.

$$2C_8H_{10}O_3 + C_9H_{12}O_3 = C_{25}H_{26}O_9 + 3H_2$$
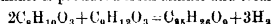
The oxygen necessary to remove the hydrogen is obtained from the atmosphere, as in a closed vessel no such change as the above takes place. Eupittonic acid appears to be dibasic, the sodium and barium salts, $C_{25}H_{24}Na_2O_9$ and $C_{25}H_{24}BaO_9$, have been prepared. Paper steeped in a solution of the acid and dried, is a most sensitive test for free alkalis on account of the blue colour of the alkaline salts of eupittonic acid. Hydrochloric acid, however, produces the same blue colour. With acetic anhydride, a diacetyl derivative, $C_{25}H_{24}O_9(C_2H_3O)_2$, m.p. 265°, is produced, which, curiously, is insoluble in alkalis, although its molecule ought to contain four hydroxyl groups.

The dibenzoyl derivative $C_{25}H_{24}O_9(C_7H_5O)_2$ forms golden needles, m.p. 232° ; the dimethyl ether $C_{25}H_{24}Me_2O_9$ has m.p. 242° ; the diethyl-ether $C_{25}H_{24}Et_2O_9$ has m.p. 201°–202° ; and the iodo compound $C_{25}H_{26}O_9I_4$ forms brown shining prisms.

Eupittone black, noreupittone, hexaoxyaurin $C_{19}H_{14}O_7$ or $[C_6H_2(OH)_3]_2C : C_6H_2(OH)_2 : O$ is formed by adding eupittone to sulphuric acid

at 140°, and keeping the temperature at 125° until the mass is pure blue; it is a dark shining black powder, and dyes mordanted fibres through a dirty violet to a deep black; the hydrochloride $C_{16}H_{14}O_7.HCl,C_2H_6O$ is deep blue (Liebermann and Widermann, Ber. 34, 1033).

EUPNINE. Trade name for a preparation of caffeine and iodine.

EUPORPHINE. Trade name for apomorphine methyl bromide.

EUPYRIN v. SYNTHETIC DRUGS.

EUQUININE. Trade name for quinine ethyl carbonate.

EUREKA v. NICKEL.

EURESOL. Syn. for resorcinol monoacetate.

EURHODINES, EURHODOLS v. AZINES.

EUROBIN. Trade name of a pharmaceutical preparation consisting mainly of the diacetate of chrysarobin (q.v.).

EUROPHEN v. SYNTHETIC DRUGS.

EUROPIUM. Eu = 152 (cf. Urbain and Lacombe, Compt. rend. 1904, 138, 637, and Jantsch, ibid. 1908, 146, 473).

Source.—The oxide of this extremely rare element is present in very small amounts in monazite sand, and is extracted from this mineral in the fraction containing the yttrium earths.

Extraction.—In separating europium from its associates, advantage has been taken of the isomorphism existing between the double nitrates of bismuth and those of the metals of the rare earths.

Bismuth nitrate gives rise to a series of double salts having the general formula

$$3M^{II}(NO_3)_2,2Bi(NO_3)_3.24H_2O$$
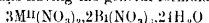
where the bivalent metal may be magnesium, zinc, nickel, cobalt, or manganese (Urbain and Lacombe, Compt. rend. 1903, 137, 568). Magnesium bismuth nitrate

$$3Mg(NO_3)_2,2Bi(NO_3)_3.24H_2O$$
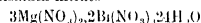
is isomorphous with the corresponding double magnesium nitrates

$$3Mg(NO_3)_2,2M^{III}(NO_3)_3.24H_2O$$
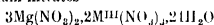
where M^{III}=Ce, La, Nd, Pr, Sm, Eu, Gd, and Tb

To a mixture of these metals in the form of their double magnesium nitrates is added a large excess of magnesium bismuth nitrate. When the product is crystallised methodically from nitric acid solution, the double magnesium nitrates of cerium, lanthanum, praseodymium, neodymium, and samarium first separate, followed by the double salt of bismuth, leaving europium and gadolinium in the mother liquors. As the fractional crystallisation proceeds, the rare earths yielding double nitrates less soluble than the bismuth double salt, are gradually eliminated until at a certain point the middle fractions contain no other tervalent metal than bismuth. When this point is reached, all the samarium has been crystallised out, and thus separated from the europium and gadolinium. The bismuth still in solution is removed from the mother liquor by hydrogen sulphide, and the europium and gadolinium separated by further fractionation of the filtrate, the europium double nitrate being the first to crystallise from this solution (Demarçay, Compt. rend. 1900, 130,

1019, 1469; Urbain and Lacombe, ibid. 1904, 138, 627). This crystallisation process is a satisfactory method for obtaining pure europium, samarium, and gadolinium, and affords a means of separating quantitatively europium and samarium (cf. Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374; James and Robinson, J. Amer. Chem. Soc. 1911, 33, 1363).

Europia (*Europium oxide*) Eu_2O_3, obtained from the purified double salt, shows no samarium spectrum, and only the strongest lines of gadolinium (Demarçay, Compt. rend. 1901, 132, 1482); it has a pale pink tint, but when produced by heating the sulphate at 1600°, the colour is somewhat deeper.

Europous chloride $EuCl_2$ is a colourless amorphous substance, forming a neutral solution in water, which oxidises at 100°:

$$12EuCl_2 + 3O_2 = 8EuCl_3 + 2Eu_2O_3$$
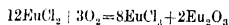
Europium sulphate $Eu_2(SO_4)_3,8H_2O$ forms pale-pink crystals, stable in air and dehydrated completely at 375° (Compt. rend. 1904, 138, 627).

The europium salts yield pale-pink solutions and in strong nitric acid they exhibit an absorption spectrum consisting of eight somewhat faint bands.

The spark spectrum is characteristic, and was first observed by Lecoq de Boisbaudran in that given by crude samaria, three very intense lines in the blue being ascribed by him to a new earth Z_{ζ}. The reversion spectrum shows the band $\lambda 615$ referred by de Boisbaudran to the earth Z_{ζ} (Compt. rend. 1893, 116, 674; 117, 199).

The most intense lines of the arc spectrum are very characteristic, and constitute a delicate test for europium, which can be thus identified in the crude oxides from monazite after removing the cerium (Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374). The cathode phosphorescence spectrum exhibits the anomalous ray referred by Crookes to the 'meta-element' S_δ. Pure europia, however, give no phosphorescence spectrum unless diluted with some other earth. With lime in the proportion $Eu_2O_3 : 99CaO$, a red phosphorescence is observed, and similar effects are obtained on mixing europia with alumina or gadolinia. Mixtures with excess of the latter give a white, and with excess of europia a red phosphorescence (Urbain, Compt. rend. 1906, 142, 205, and Seventh Congress of Applied Chemistry, 1909, section 10, 94).

(Ultra-violet and arc spectra, v. Exner and Haschek, Sitzungsber. Wien. Akad. 1902, IIa, 3, 42, and Die Wellenlangen' der Bogenspektra, 1904).

Europium has been detected spectroscopically in the sun's chromosphere, in α-Boötis and in β-Geminorum (Lunt, Proc. Roy. Soc. 1907, A, 79, 118). G. T. M.

EUROSAMARIUM. An element detected by Eder, and occurring associated with europium and gadolinium in monazite (Sitzungsber. K. K. Akad. Wiss. Wien. 1917, IIa, 126, 473).

EUSCOPOL. Syn. for inactive scopolamine hydrobromide.

EUSOL. An antiseptic, used in surgery, consisting of a solution prepared by shaking up in 1 litre of water 25 grams of a mixture of equal weights of chloride of lime and boric acid, and filtering off the sediment; the solution

contains about 0·54 p.c. of hypochlorous acid, and 1·28 p.c. of calcium biborate.

EUSTÉNIN. Trade name for an addition product of theobromine-sodium and sodium iodide.

EUSYNCHITE v. VANADIUM.

EUXANTHIC ACID, EUXANTHONE, and **EUXANTHONIC ACID** v. INDIAN YELLOW.

EUXENITE. A rare-earth mineral consisting essentially of columbate and titanate of yttrium and erbium, with smaller amounts of uranium, thorium, cerium earths, iron, &c. Crystals are orthorhombic, but are very rare and indistinctly developed ; the mineral is more often massive, with a blackish-brown colour and a brilliant pitchy lustre ; sp.gr. 4·6–5·1 ; H. 6½. In appearance and character, it closely resembles several other rare-earth minerals, particularly polycrase, from which it differs in containing a lower ratio of $(Cb,Ta)_2O_5 : TiO_2$. It is occasionally found in the felspar quarries at several places in the neighbourhood of Arendal in Norway (v. W. C., Brögger, Die Mineralien der Südnorwegisschen Granit-Pegmatitgange, 1906) Also in the pegmatite veins of Madagascar, Cooglegong in Western Australia, South Sherbrooke in Ontario, &c Named from εὔξενος, friendly to strangers, in allusion to the several rare-earths it contains. L J. S.

EVAPORATION. The term ' evaporation ' is used in connection with technical or manufacturing operations where a liquid is converted into vapour, but in chemical manufactures it is generally limited to those processes where the object is to separate a liquid from a solid which is dissolved in it, or to separate a more volatile from a less volatile liquid. In cases where the liquid to be evaporated is one of the products of the process, and is collected by condensation, the process is known as DISTILLATION (q.v.). Where a solid substance contains water, not as water of crystallisation, and without presenting visible moisture or wetness, the process of removing this moisture under suitable circumstances is known as DESICCATION or DRYING (q.v.). The operation of evaporation, however, is conducted on the greatest scale in the generation of steam for steam engines, and in the production of steam generally for manufacturing purposes. Although more water is evaporated in connection with the steam engine than for any manufacturing processes, yet great quantities of steam are used as a convenient means of applying and distributing heat, especially when regulated and moderate temperatures are required. In such cases the heat is applied to the vessel to be heated by jacket spaces or through coils of pipes immersed in the liquid to be raised in temperature. Such applications are made in sugar and confectionery manufacture, and in distilleries, breweries, and dyeing, &c.

Water and many other liquids evaporate without the application of heat. A vessel of water freely exposed at the ordinary temperature of the atmosphere soon evaporates and disappears. This is due to the fact that water vapour has a sensible pressure at ordinary temperatures, and as gases and vapours freely diffuse throughout each other, any water placed with a free surface in a confined space continues to evolve and diffuse its vapour until the water vapour present in the whole space is at

the maximum pressure which corresponds with the temperature. Although evaporation occurs in this way without any application of increased temperature, yet heat is absorbed by the vapour formed from the liquid, and if the evaporation be rapid and be conducted under such circumstances that heat from surrounding objects is prevented from reaching the liquid, then its temperature will be greatly reduced. This fact is illustrated by the well-known lecture experiment of placing a shallow copper cup filled with ether upon a block of wood, and under it a drop of water. When air is blown upon the ether it rapidly evaporates and carries off so much heat from the copper that the water drop under it is frozen and the copper adheres to the wood. A liquid is said to be volatile when its vapour has a considerable pressure at ordinary atmospheric temperatures. At 20°, for example, the pressure of water vapour (or tension as it is somewhat inappropriately called) is 17·39 mm. mercury, whilst the pressure of ether vapour at the same temperature is 433·3 mm. and that of alcohol 44·5 mm. If the liquids be placed in atmospheres whose pressures could be kept at these points by artificial means, then these liquids would boil. As the evaporation under these circumstances is very rapid, relatively to the flow of heat to the liquid from surrounding bodies, if only atmospheric temperature be available, the heat is abstracted so quickly that many liquids freeze.

Advantage is taken of these properties for many purposes in the use of air currents passed over the surfaces of liquids to evaporate them without the application of other than natural heat. Reduced pressures are also applied to evaporate without heating or to reduce the temperature necessary in order to avoid chemical decomposition and also to produce cold mechanically.

Evaporation in steam boilers. The evaporative efficiency of the steam boiler has been more closely studied than that of any other type of evaporating apparatus, and the principles of the economical application of heat for evaporating are more completely known in this connection than in any other.

The leading types of steam boilers now in use for the purposes of motive power are as follows : Lancashire, Cornish, Locomotive multitubular, Marine multitubular, and Water-tube or tubulous types.

Obviously in an article of this character detailed description of the various types of boiler is uncalled for ; the reader is therefore referred to the numerous text-books existing on the subject, such, for example, as "Steam-Boiler Construction," by W. S. Hutton ; "Steam-Boilers, Their History and Development," by H. H. P. Powles ; "Steam-Boilers," by C. H. Peabody and E. F. Miller.

Evaporation in open vessels. In many chemical manufactures it is necessary to evaporate off water in which the substance, object of the process, is dissolved, and in such cases, when heat is to be applied, it is desirable to economise fuel to the greatest possible extent. The heat of waste gases is therefore used as much as possible. The method of applying heat varies considerably with the chemical nature of the substance dealt with, and choice of economical apparatus is often limited by the corrosive nature

of the liquid to be evaporated. In the process of concentrating oil of vitriol from the dilute acid, a series of shallow open lead pans receives the diluted acid and heat is applied below. The hot furnace gases are allowed to impinge upon the bottom of the vessel containing the weakest acid, and therefore requiring the greatest quantity of heat for evaporation, and as the gases cool they impinge upon the succeeding vessels of stronger and stronger acid, requiring less quantity of heat until the acid has become as concentrated as it is safe to trust to leaden vessels. Instead of this plan, in some cases the furnace gases are passed over the surface of the acid in order to heat it from above, and the volume of gases in motion removes the vapour as fast as it is formed. The advantage of surface evaporation arises not from the fact of its being economical, because liquids are heated with difficulty from above. The hot liquid in contact with the gases expands and has no tendency to cause convection currents, but rather remains stationary above the colder portions, and accordingly it is always advisable to heat from below when possible. In many processes, however, during evaporation, a deposit comes down and this, coating the bottom of the vessel, prevents the free contact of the metal with the liquid. The resistance to the passage of heat from the metal to the liquid is thereby much increased, and the bottom suffers rapid destruction from over-heating. In boilers using very hard water this is a fruitful source of trouble and danger.

When surface evaporation is resorted to, large surfaces are exposed in shallow tanks over which the flame and hot gases from a furnace are allowed to pass. The pans are covered in so that the radiant heat from the brickwork assists the action of the flame and hot gases. Arrangements of this kind are used in evaporating weak alum liquors, and the tanks are built up of bricks bound together with a cement composed of lime and alum shale. Sometimes an open pan is placed above the gases to contain the feed liquid and heat it in its progress to the evaporating pans.

Evaporation of brine. Brine is sometimes evaporated by allowing the liquor from the springs to flow over masses of twigs in such a manner as to expose very extensive surfaces to the action of air currents; by pumping over a succession of these surfaces it is gradually concentrated. When artificial heat is applied to the evaporation of brine, large shallow salt pans are used. They consist of flat quadrangular vessels of plate iron supported upon suitable brick walls, forming flues which distribute the heat from furnaces placed in the centre part under the vessel. The flames strike directly upon the bottom of the vessel, and the hot products of combustion are conducted outwards by flues leading to the stack or chimney. In this way they traverse the whole bottom surface of the evaporating pans. The pans are of great area, often 60 feet long by 30 feet wide. The water vapour is collected by a large conical hood and carried off by a separate chimney. The sides of the lower part of the cone are so constructed that they can be opened to admit air from the direction in which the wind is blowing. This assists the evaporation by carrying off the water

vapour generated and exposing the surface to a continual air current.

If heat enough to cause a liquid to boil be applied, an air current will not increase the evaporation, but will tend to diminish it by cooling the vessel containing the liquid; but when the liquid does not reach the boiling-point, the continuous removal of the atmosphere in contact with the liquid is necessary. If this be not done, then, so soon as the atmosphere has become saturated with the vapour, that is, so soon as the water vapour is present in quantity sufficient to produce the pressure which corresponds with the temperature of the liquid, the evaporation ceases.

It is a necessary condition of evaporation at temperatures less than the boiling-point, that the atmosphere into which the evaporation takes place should be continuously renewed, and it is advisable that the air into which the water evaporates should not be of lower temperature than the liquid. When the temperature of the air is lower than that of the liquid, the volume of vapour carried off is much reduced, as the air must be heated by the vapour before it is capable of carrying off the volume equivalent to the vapour pressure. Producer gas is used for evaporating the brine at Ischl salt works, and the operation is conducted in deep rectangular plate-iron vessels grouped together, and fed continuously by a system of distributing pipes.

Steam is much used to supply the heat required for evaporation, especially when the substances to be dealt with are of an easily decomposable nature if overheated. The heat is often applied to the vessel by means of a steam jacket, that is, the vessel is made double walled, and the interspace is utilised to receive the hot steam. When the temperature requires to be higher than 100°C., the jacket space is constructed to withstand pressure, and steam under boiler pressure is supplied, but steam is most commonly used at atmospheric pressure and applied to the liquid by passing through rows or coils of pipes immersed in it. The arrangement of these pipes varies, and in some cases they are so connected as to be capable of hinging out of the vessels for ready access and cleaning purposes.

Milk is now rapidly evaporated by spraying into heated air without raising the milk temperature to such a point as would cause chemical change.

Evaporation under reduced pressures. In the older processes of sugar manufacture, the sugar liquors were concentrated by the direct application of heat from a fire upon the vessels containing them, but the greatest difficulty was experienced in preventing decomposition when the solution became concentrated. To avoid this difficulty, the vacuum pan was introduced by Howard, and in various modified forms it is still used. The boiling-point of a liquid depends upon the pressure to which it is subjected, and by reducing the pressure the boiling-point is greatly reduced. The vacuum pan consists essentially of a globular copper vessel containing the sugar liquor, and having the lower portion steam jacketed, while steam also passes through a coil of pipe immersed in the liquid. The upper part of the vacuum pan carries a circular

steam dome or cylinder from which a pipe passes to a vessel intended to collect any liquor which may have primed over. From this vessel it is run back into the pan again. An air pump exhausts the apparatus and passes the steam to a condenser of usual construction. Fig. 1 shows a vacuum pan made by Messrs. Manlove, Alliot, & Co. The vacuum pan A is formed in two portions bolted together. It is fed with liquor from the vessel B by suitable cocks, the pipe connections a, b being arranged to equalise the pressure within the vessel, so that the flow may be towards A. The live steam is admitted at the valve C, and passes through coil D into the jacket E, from whence it discharges and drains by the pipe F. The cylindrical dome or cylinder G prevents any great priming, but any liquid which may find its way by the pipe H is caught in the cylinder I and returned to A by the pipe K. The pipe L leads to the air pump and condenser.
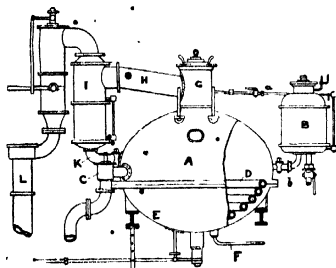
Fig. 1.

A thermometer placed in the upper part of the pan indicates the temperature of the operation, whilst a vacuum gauge or barometer column is used to show the pressure within. The boiling-point of the liquid at atmospheric pressure is about 250°F., and this is reduced to 150°F. by using the vacuum pan.

Fig. 2 shows a vacuum pan of modern construction, made by the Mirrlees Watson Co., Ltd., of Glasgow. In this vacuum pan, the liquor is heated in the vessel a by coiled steam pipes b, and also by reason of its passing upwards through small tubes c, through a steam chamber, d, the down flow of the liquor taking place through the central large tube e. In other respects, the operation of this vacuum pan is similar to that shown in Fig. 1.

Evaporation under reduced pressure by triple and multiple effect. It is evident that as a liquor becomes more concentrated the boiling-point rises, and in evaporating liquids liable to chemical change by overheating, the pressures under which boiling is effected must be arranged to keep the temperature within safe limits. In the case of sugar liquor this safe limit is 227°F. Steam at 5 lbs. per square inch above atmosphere has this temperature, and if it be applied to a pan containing a weak sugar liquor at atmospheric pressure, the liquor will boil.

Neglecting losses by radiation and like causes, the steam coming from it has the same amount of heat as was imparted to the liquor by the steam under slight pressure, and if it be

conducted to the coil and jacket of a second pan in which a slight vacuum is maintained, it will generate almost its own weight of steam at lower pressure and temperature, and so evaporate the water from the second pan. If the steam so generated be taken to the coil and jacket of a third pan, its heat can again be utilised to evaporate the liquor there, provided the vacuum is sufficient to allow it to boil. This process may be continued until the original heat of the steam supplied to the first pan is dissipated by conduction and radiation. This is the principle of the ' triple-effect ' apparatus, by which a great economy is effected in the amount of fuel needed to evaporate a given weight of liquor. The steam from one pan at higher pressure proceeds to the coil and jacket of the next, and the steam from the second proceeds to the coil and jacket of the third, the pressures within the pans proceeding in descending order as well as the temperatures.

Fig. 3 is an illustration of a triple-effect evaporator of the ' Hagemann ' type, constructed by the Mirrlees Watson Co., Ltd., for concentrating sugar. In this evaporator, the liquor is fed through an internal perforated pipe D at the bottom of the vessel A, and the flow of liquid from vessel to vessel is automatically regulated by traps E, the liquor passing through the vessels A, B, and C in turn, the reduction in pressure being so arranged that it is least in A, more considerable in B, and greatest of all in C, so that the boiling-points are lower in each succeeding vessel. The heating surface is obtained by means of a number of vertical tubes F, through which the liquor passes, these tubes being arranged in a steam or vapour space, G, divided by horizontal baffle plates H. The steam enters the steam space at the top above the upper baffle plate, and passes to the intermediate and lower spaces through apertures in the baffle plates slightly larger than the tubes which pass through them, the rush of steam through the openings removing the water of condensation from the surface of the tubes, and improving their efficiency. The upper part of each vessel acts as a separator, the vapour escaping, past a baffle J to prevent priming, through an outlet K either to the next effect or to the condenser.

In the Kestner ' climbing film ' evaporator, one complete section of which is illustrated in Fig. 4, vertical tubes are also used for the passage of the liquor, but they are fewer and of greater length than in the apparatus last described. Steam supplied through an inlet A to a jacket B causes ebullition of the liquor, supplied to a tank C, releasing a volume of vapour in the tubes D which occupies the central portion of each tube and carries up a film of the liquor on the internal surface. A fixed baffle E, by means of suitably shaped vanes, produces a whirling motion of the liquor and vapour mixture as it emerges into the separator F, whereby the liquor is thrown outwards and drawn off through an outlet G, and the vapour escapes, through a ' save-all ' H, by an outlet J. In another form the separator is placed at the bottom of the apparatus, the liquor, after passing through the ' climbing film ' tubes, being conducted thereto by a set of ' falling film ' tubes also within the steam jacket B.
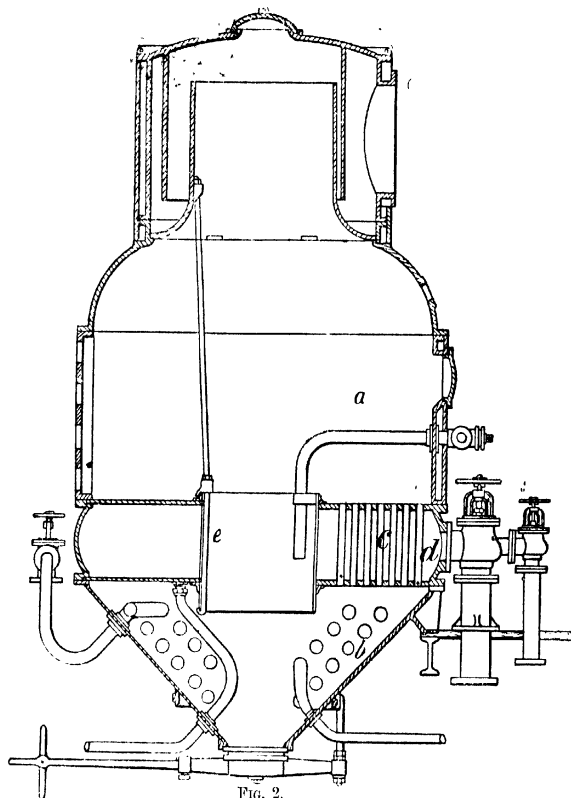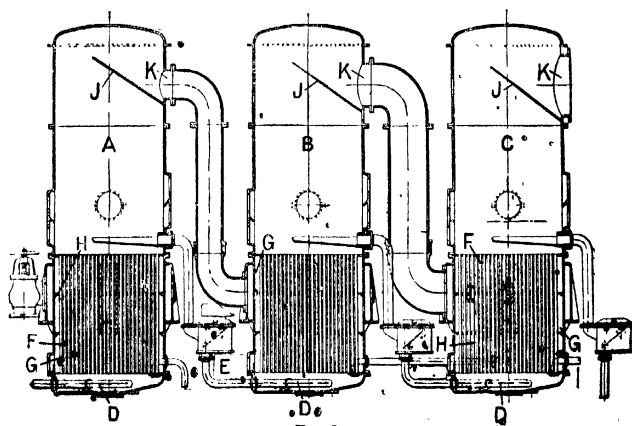
Fig. 2.

Fig. 3.

Any number of sections as described may be connected to form a multiple effect apparatus, the liquor and vapour from the outlets G and J of one section being respectively led to the tank C and inlet A of the next.
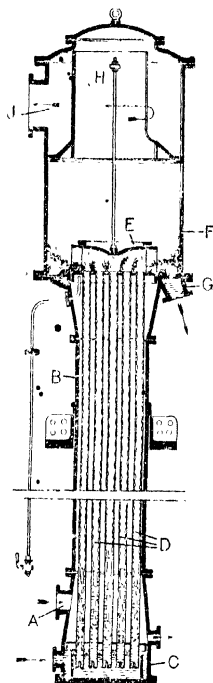

FIG. 4.

The Yaryan evaporator. This ingenious evaporator is the invention of H. T. Yaryan, of Ohio, U.S.A., and it is now largely used in this country, the Continent, and America. It utilises evaporation under reduced pressures as with the triple effect and also multiple effect. It differs from other inventions of the same class in the method of applying heat to the liquid to be evaporated, whereby the liquid is heated in small quantities at a time, and is brought into very effective contact with the heating surfaces. Instead of using coils immersed in a liquid which is also heated by jacketed surfaces, the heat is applied by steam to the exterior surfaces of tubes, and the liquid to be evaporated is pumped within these tubes. The tubes are arranged in straight cylindrical drums, and pass from end to end, terminating in chambers with partitions so placed that when the liquid is pumped in at one end of a series it must pass through the whole series before escaping into the separating chamber. Fig. 5 is a section of

one drum of the evaporator, showing that the liquid is pumped in at one end, travels along in the direction of the arrows, and finally escapes with the steam which is generated into the separator. The tubes are divided into sections termed ' coils,' and each section consists of fine tubes coupled at the ends so as to form a continuous passage. The liquid and vapour pass from section to section in series, and so come into effective contact with the whole surface. As the liquid is pumped in it evaporates, and the steam produced carries it forward through the tubes, so that a mass of liquid and steam is brought in contact with every part of the whole heating surface, moving at a high velocity because of the steam generated, which has only the one direction of escape, that is, through the whole system of tubes in each towards the separator. The liquor under treatment issuing from the last set of tubes into the separator falls to the bottom, as shown in Fig. 5, and the vapour rising up flows in the direction of the arrow to the *catch all*, where any liquor entrained is caught during its passage through the number of small tubes with which this vessel is fitted,
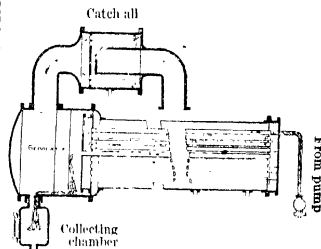

FIG. 5.

and, striking against the end cover, falls to the bottom and is drained off into a receiver. This ensures dry vapour being passed on to the evaporating shell of the next vessel, where it in turn boils the liquor which is inside the tubes, and so on through the various effects until the vapour from the last vessel reaches the condenser. The advantages of this apparatus are its economical working and rapid flow of the liquor under treatment. Only a small quantity of liquid is in the apparatus at one time, and so it is exposed to heat for a much shorter period than in the ordinary vacuum pan, which is an important point. The apparatus avoids entirely the loss of colour which always occurs to some extent in the older vacuum pans because of the long period of time taken to evaporate the large quantity of liquid they contain, amounting in some cases to thousands of gallons. The Yaryan evaporator can be started very rapidly, as it contains but a small mass to be heated. At the same time, the details are arranged to permit of ready access to the tubes and ready cleaning. This is greatly assisted by the fact that the tubes are straight. Fig. 6 shows a quintuple-effect evaporator with its vacuum and auxiliary pumps in general use, for soda ash recovery in paper mills, caustic soda, caustic potash, meat extract,

distillery refuse, and other liquids readily amenable to concentration.

According to the patentees of the Yaryan apparatus, their double effect will evaporate
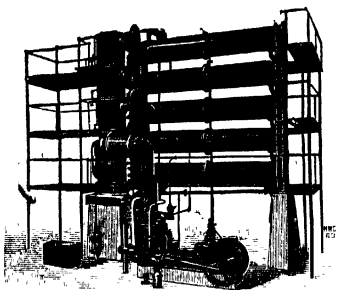

FIG 6.

16 lbs. of water for every pound of coal consumed under the boiler, 23½ lbs. in a triple effect, 30½ lbs. in a quadruple effect, assuming that the boiler is so constructed as to evaporate 8½ lbs. of water per pound of coal.

The Yaryan apparatus has, since its first introduction in 1888, been greatly improved in design and efficiency, and large sextuple-effect apparatus working on the Yaryan principle have been constructed by the Mirrlees Watson Co., Ltd., for the distillation of fresh water from salt water, producing from 25 to 350 tons per day of 24 hours, and also for use in the Solvay process of soda manufacture in Europe and America. Fig. 7 indicates the essential features of such an apparatus for the distillation of salt water. Salt water, previously warmed by being passed through heaters, is supplied by a pipe A to heating tubes in the lowest evaporator B_6, and thence is passed in succession by means of pipes c through heating tubes in the remaining evaporators. It has then reached boiling-point, and is circulated through the evaporating tubes of the first evaporator B_1, to which boiler steam is supplied by a pipe D. The mixture of liquor and vapour is conducted from the evaporators B_1-B_6, to the respective separators E_1-E_6, by pipes F, the outlets for the liquor and vapour from each separator to the next evaporator stage being by pipes G and H respectively. Concentrated brine is drawn off from the last separator E_6 by a pipe J, and the condensed fresh water passes from stage to stage by pipes K, and is finally drawn off through an outlet L.
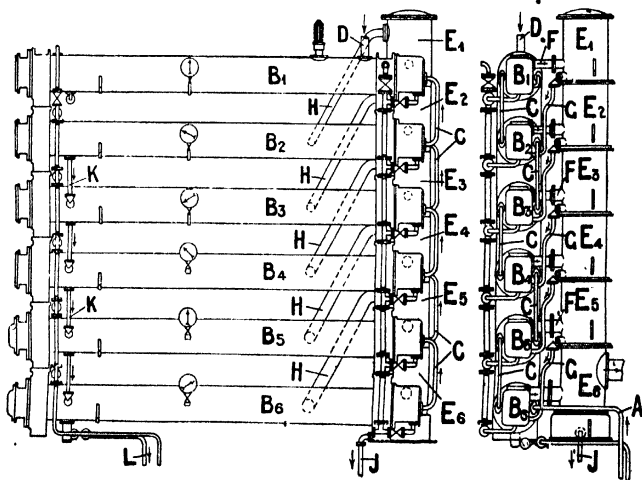
In the Lillie type of evaporator the tubes are

FIG. 7.

also arranged horizontally, but the steam is passed through them and the liquor is allowed to fall over their external surfaces.

Evaporation in mechanical refrigerators. A separate class of mechanical refrigerators exists in which the cooling or refrigerating effect is produced by evaporation. Liquids used are ether, anhydrous ammonia, and anhydrous sulphur dioxide. In all of these the process of the machine is identical. The volatile liquid is

introduced into a chamber at a pressure at which it is liquid, and the vapour is rapidly withdrawn from the vessel by a pump. The rapid evaporation absorbs heat so quickly that the temperature falls and a brine or other liquid is cooled within a coil of pipes immersed in the liquid. By circulating this brine, the low temperature may be utilised for reducing the temperature of a cold store room or for producing ice.

The vapour drawn off by the pump is compressed and cooled by passing through tubes surrounded by water, and so becomes liquid again. It is then injected into the evaporating chamber again, so that the process is practically continuous, and but slight renewal of the volatile liquid is necessary to make up for small leakages.

The same principle is applied in Carre's freezing machine for freezing water. In this case the vapour is removed from the surface of the water by a pump and condensed by strong sulphuric acid. Ammonia is also utilised in another apparatus in solution in water for the same purpose. By alternate expulsion from the water and absorption, cold is obtained.

The rapid evaporation of liquid carbonic acid, air, and other bodies which are gaseous at normal temperatures and pressures, has also been used to produce low temperatures by liquefying the more permanent gases. D. C.
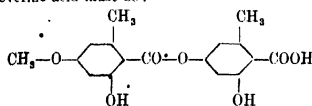
EVERNIC ACID and **EVERNINIC ACID.** Evernic acid, or *lecanoric acid monomethyl ether*, was first isolated by Stenhouse from the *Evernia prunasti* (Annalen, 68, 83), and has been found also by Hesse (Ber. 1897, 30, 366) to exist in the *Ramalina pollinaria* (*cf.* also Zopf, Annalen, 1897, 297, 271).

The lichen is extracted with diluted milk of lime, the extract neutralised with acid, the precipitate collected, dried, and digested with a little boiling alcohol. The hot alcoholic liquid, treated with its own volume of water, deposits crystals of evernic acid (Stenhouse).

Evernic acid crystallises in small colourless needles, m.p. 168°–169°, readily soluble in hot alcohol, and when boiled with solutions of the alkali hydroxides or baryta water, gives CO_2, orcinol, and *evernic acid*

$$C_{17}H_{16}O_7 + H_2O = C_9H_{10}O_4 + C_7H_8O_2 + CO_2$$

Ramalic acid suffers a similar decomposition.

Fischer (Ber. 1913, 46, 3253 ; and 1914, 47, 505) showed that when evernic acid was methylated by means of diazomethane, in ethereal solution, a neutral crystalline ester identical with trimethyl-lecanoric acid methyl ester was obtained, and he pointed out that, as the methoxy group in everninic acid is in the para-position to the carboxyl group, the structure of evernic acid must be :

CH₃—O—⟨CH₃⟩—CO—O—⟨CH₃⟩—COOH
            OH   OH

From this it follows that the isomeric ramalic acid (*v.* Ramalic acid) may be expressed as :

HO—⟨CH₃⟩—CO—O—⟨CH₃⟩—COOH
       OCH₃   OH

or HO—⟨CH₃⟩—CO—O—⟨CH₃⟩—COOH
        OH   OCH₃
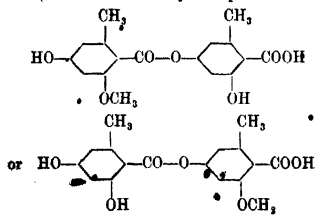
* For descriptions of the Na, Ba, Ca, Cu, Pb, and Ag. salts of evernic acid, *cf.* Hesse (J. pr. Chem. 1915, [ii.] 92, 425).

Diacetyl-evernic acid $C_{17}H_{14}O_7Ac_2$ is a crystalline powder, m.p. 144°.

Everninic acid (orsellinic acid monomethyl ether) resembles benzoic acid in appearance, melts at 157°, and yields the ethyl ester
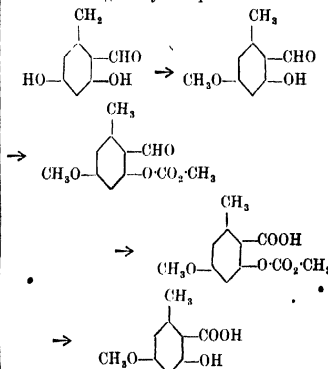
$$C_9H_9O_4(C_2H_5)$$
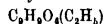
m.p. 72°. By digestion with hydriodic acid, everninic acid gives orcinol, CO_2, and 1 molecule of methyl iodide. According to Heinrich (Ber. 1904, 37, 1406), two formulæ are possible for everninic acid :

(1) ⟨CH₃ / COOH / OCH₃ / OH⟩   (2) ⟨CH₃ / COOH / OH / OCH₃⟩
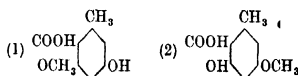
Fischer and Hoesch (Annalen, 1912, 391, 347) have, however, shown that *orsellinic acid a-methyl ether*, prepared by them, and which has the structure (2), is identical with everninic acid.

This conclusion has been further substantiated by the synthesis of *everninic aldehyde*, m.p. 65°C. (and from it of everninic acid) (Hoesch, Ber. 1913, 46, 886), by the careful methylation of orcyl aldehyde with methyl sulphate, and 2N caustic soda in the presence of acetone. This when treated with an acetone solution of methylchlorocarbonate, yielded *methylcarbonato-everninic aldehyde*, needles, m.p. 77°C., and the latter, when oxidised with potassium permanganate, was converted into *methylcarbonato-everninic acid*, needles, decomposing at about 100°C., which on hydrolysis with N caustic soda solution yielded everninic acid. These changes may be represented thus :

HO—⟨CH₂ / CHO / OH⟩ → CH₃O—⟨CH₃ / CHO / OH⟩

→ CH₃O—⟨CH₃ / CHO / O·CO₂·CH₃⟩

→ CH₃O—⟨CH₃ / COOH / O·CO₂·CH₃⟩

→ CH₃O—⟨CH₃ / COOH / OH⟩

Hesse (J. pr. Chem. 1915, [ii.] 92, 425) has described the following derivatives of everninic acid :—

Acetyl everninic acid $C_9H_9O_4Ac$, colourless prisms, m.p. 111°C.

Nitro-everninic acid, orange-red needles, m.p. 195°C.

Dinitro-everninic acid $C_9H_8O_4(NO_2)_2H_2O$ golden-yellow needles, m.p. 87°C.—the potassium salt is very explosive.

Hesse's expression (J. pr. Chem. [ii.] 57, 253) of the isomerism of evernic acid and ramalic acid, and which was based upon the older formula of orsellinic acid, is as follows :
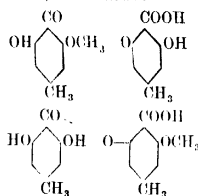
A. G. P. and A. E. E.

EVERNIIN *v.* GUMS.

EVODIA MELIÆFOLIA. This tree, belonging to the *Rutaceæ*, is found in China and Japan, where its bark is largely employed in dyeing and in medicine. It was formerly described by Loureiro as *Pterocarpus flavus*, but this error was eventually corrected by P. W. Squire (Pharm. J. 1888, [3] 18, 785), who showed it to be really *Evodia glauca*, which is synonymous with *E. meliæfolia*. By qualitative tests, Martin, Tokio (Arch. Pharm. 1898, 13, 337) and Squire (*l.c.*) suspected the presence of *berberine*, and this colouring matter was subsequently isolated by Perkin and Hummel (Chem. Soc. Trans. 67, 415).   A. G. P.

EVODIN $C_{17}H_{20}O_6$. A crystalline substance found in the fruit of *Evodia rutaecarpa*, used in China and Japan in medicine and perfumery. First isolated by Kermatzu by treatment of the dried fruits with benzene ; m.p. 285°. Insoluble in water, alcohol, ether, and light petroleum, slightly soluble in hot benzene, ethyl acetate, and chloroform, soluble in acetic acid and alkali solutions (*cf.* Asahina and Ishio, J. Pharm. Chim. 1916, [viii] 13, 53).

EXALGIN. Trade name for methyl acetanilide (*v.* SYNTHETIC DRUGS).

EXODIN *v.* SYNTHETIC DRUGS.

EXPLOSION, GASEOUS. Within recent years there has been an enormous increase in the extent to which the internal combustion engine has been utilised, and there are now many millions of h.p. at work on this principle. Gas engines using coal gas, producer gas, or blast-furnace gas, are now working for all powers up to 2000 h.p. per cylinder, and a large number of heavy oil engines are also in use. In addition, there are many thousands of petrol motors at work.

In internal combustion engines working on the constant volume cycle, the motive power is produced by the explosion of mixtures of inflammable gas or vapour and air in certain proportions, and the pressure produced by the explosion is utilised to propel the piston of an engine, as is done by the steam pressure in a steam engine.

Seeing that a proper understanding of the phenomena associated with gaseous explosions is necessary, not only for persons in charge of internal combustion engines, but also for those responsible for the safety of workers both in coal mines and in factories where explosive mixtures may be encountered or used, it is desirable first to consider generally the properties of such mixtures and the mode in which flame is propagated through them. At the outset, it should be recognised (1) that, under given conditions of temperature and pressure, the "*range of inflammability*" of mixtures of any particular combustible gas and air (or oxygen) may be strictly defined, so that all mixtures outside of certain 'lower' and 'upper' limits are non-inflammable ; (2) that the *ignition* of any given inflammable mixture at a particular pressure is determined by the attainment of a certain definable thermal (or electrical) condition at some point or region in it ; (3) that after ignition the speed and mode of propagation of flame through the mixture are usually capable of measurement or analysis by well-established experimental methods ; and (4) that when such a mixture is inflamed in a closed vessel, the maximum pressure attained on explosion may be accurately determined. But notwithstanding the truth of this statement, it is needful to warn the reader against errors involved in the loose employment of such terms as '*ignition temperature,*' '*speed of inflammation or flame propagation,*' '*pressure of explosion,*' etc , unless the concomitant physical circumstances are simultaneously defined.

A —IGNITION PHENOMENA.

Chemical change may be determined in a gaseous explosive mixture at a much lower temperature than is required to develop flame in it. Thus, for example, if electrolytic gas be heated in an enclosure to a temperature somewhat higher than 400°, the formation of steam can usually be detected after a lapse of a few days. On gradually raising the temperature the rate of interaction between the hydrogen and oxygen rapidly increases until at length a point would be reached when the rate at which heat is lost from the system (*e.g.* by conduction through the walls of the enclosure) is more than counterbalanced by the rate at which it is developed by the interaction. The reaction would then become self-propellant.

The temperature at which such autogenous (or self-propellant) reaction begins in a given gaseous mixture is usually termed its '*ignition temperature*' or '*ignition point,*' although it is not ordinarily a well defined physical constant, being dependent, for example, upon the manner in which heat is conveyed to the mixture. It is clear also that the ignition temperature, as thus defined, does not necessarily correspond with the appearance of flame in the mixture. There is, indeed, usually a definite '*pre-flame*' period, the duration of which can be controlled, and which varies considerably with the different gas mixtures. Only when a mixture is fired by adiabatic compression, and the pre-flame period is negligibly short, can its '*ignition temperature*' be regarded as a physical constant and determined with precision. In most cases the ignition temperatures assigned to a series of gas mixtures merely give an approximate index of their 'relative ignitibilities.'

The Determination of Ignition Temperatures. —Several experimental methods (of which three principal ones will be hereafter described) have been used to determine the so-called 'ignition temperatures ' of gases. The results naturally differ according to the details of the method adopted, and must therefore be carefully differentiated.

(1) A common method is to pass successive samples of a particular inflammable mixture into a vessel whose temperature is gradually raised until the lowest degree at which flame appears has been found. In this way the 'relative ignitibilities' of a series of gas-air mixtures may be determined, and for such purpose the method is a useful one. Thus, for example, one of us (R.V.W.) has recently determined by this method the 'relative ignitibilities' of a series of methane-air mixtures, expressed in each case as the lowest temperatures of the particular enclosure required to inflame each mixture, as follows :—

Per cent. Methane	6·0	7·0	8·0	9·0	10·0	12·0	13·0
Temperature of enclosure	695°	698°	701°	707°	713°	726°	73..

It may be noted, in passing, that the most ignitable of these mixtures is not the one (9·45 p.c. methane) which on combustion gives the greatest heat development per unit volume, but rather those containing a considerable excess of oxygen. The method does not, however, disclose the lowest temperature at which a given mixture can be ignited, because the walls of the heated vessel, by inducing chemical combination on their surface, retard the actual appearance of flame.

(2) A better method. (first employed by H. B. Dixon and H. F. Coward, Chem. Soc Trans. 1909, 98, 514), which to a large extent eliminates the effect of heated surfaces, consists in heating the combustible gas and the air (or oxygen) separately to a known temperature and then allowing them to mingle, increasing the temperature of each gas stream, *pari passu*, until their mixture results in flame. The '*ignition temperature ranges*' of some combustible gases, at atmospheric pressure, as determined by this method, are as follows :—

Combustible Gas	Ignition Range	
	In oxygen	In air
Hydrogen	580°–590°C.	580°–590°C.
Carbon monoxide	637°–658°	644°–658°
Cyanogen	803°–818°	850°–862°
Ethylene	500°–519°	542°–547°
Acetylene	416°–440°	406°–440°
Hydrogen sulphide	220°–235°	346°–379°
Methane	556°–700°	650°–750°
Ethane	520°–630°	520°–630°

These figures record for a given gas the lowest temperature at which any mixture of it with air or oxygen would inflame. But they afford no information as to the effect of varying the proportions of the gas and air.

(3) The temperature produced by the adiabatic compression of a gaseous explosive mixture within a closed cylinder may be accurately calculated from the fundamental gas laws, and this method has been successfully employed by H. B. Dixon and his co-workers for determining the 'ignition temperatures' of various mixtures of hydrogen and oxygen, as follows :—

Mixture	Ignition Temperature as determined by Adiabatic Compression
$2H_2 + O_2$	526°C.
$2H_2 + 2O_2$	511°
$2H_2 + 8O_2$	478°
$2H_2 + 16O_2$	472°

According to Dixon and Croft's determinations by this method of the ignition-points of mixtures containing electrolytic gas, whereas successive additions of hydrogen or nitrogen progressively raise the ignition temperature of the undiluted gas by regular increments, as would be supposed, successive additions of oxygen, on the other hand, lower it, as shown in the following table : —

THE IGNITION-POINTS OF MIXTURES CONTAINING ELECTROLYTIC GAS BY ADIABATIC COMPRESSION.

(By H. B. Dixon and J. M. Crofts, 1914.)

Electrolytic Gas, $2H_2 + O_2 = 526°$					
$+xH_2$		$+xN_2$		$+xO_2$	
$x=1$	544°	$x=1$	537°	$x=1$	511°
$x=2$	561°	$x=2$	549°	$x=7$	478°
$x=4$	602°	$x=4$	571°	$x=15$	472°
$x=8$	676°	$x=8$	615°		
$(526+18x)°$		$(526+11x)°$			

The observed raising effects of successive dilutions with hydrogen and nitrogen call for no comment, save that the relative greater effect of hydrogen, as compared with nitrogen, may be attributed to its greater thermal conductivity; but the lowering effect of oxygen is indeed puzzling, and its meaning can only be conjectured. Dixon and Crofts have suggested that it may be due either to the formation of some active polymeride of oxygen under the experimental conditions (which seems doubtful), or that the concentration of oxygen in some way or other brings about increased ionisation of the combustible gas This at once raises the larger question of whether or not ignition is a purely thermal problem, as until recently has generally been supposed.

Ignition by adiabatic compression is utilised in the Diesel oil engine, and in gas engine practice pre-ignition of the charge may take place during the compression stroke if too high a compression is employed. Knowledge of the degree of compression required to cause the ignition of a particular gaseous mixture is, therefore, of considerable industrial value.

Ignition by a Source of Heat of Short Duration.—This is a very common way of igniting explosive mixtures in everyday practice, although up to the present experimental data regarding it are very meagre. It will be realised that if the inflammation of a large volume of gas is attempted by rapidly heating a small portion of it, the size and duration of the source of heat employed, as well as its temperature, will be of importance, because the effectiveness of any means of ignition depends upon whether or not the volume of mixture first inflamed communicates by its combustion sufficient heat to the adjacent layer of mixture to inflame it in its turn. In general, the shorter the duration of the source of heat employed to ignite a given gas mixture, the higher must be its temperature. Unfortunately, until now this aspect of the question has been but little explored, but the point may be illustrated by some recent determinations of the '*relative ignitibilities*' of

mixtures of various gases with air expressed in the terms of the lowest temperatures at which a hot body of minute area must be raised in order to cause immediate ignition of the particular mixture to which it was momentarily applied. Such temperatures have obviously only an empirical interest.

Gas (Mixtures with air)	Minimum temperature of hot body required for immediate ignition by momentary contact
Hydrogen . . .	747°C.
Carbon monoxide . .	931°
Ethylene . . .	1000°
Coal gas . . .	878°
Petrol (Fraction 0-80°C.)	995°
Benzene . . .	1062°
Ether	1033°

Ignition by Electric Sparks.—It is still a matter of controversy whether ignition by means of an electric spark is a thermal phenomenon, or whether there is simultaneous ionization of the mixture by the spark, the ionization playing a necessary and important part in promoting the combustion of the gases. So far as the secondary discharge is concerned, ionization of the mixture between the electrodes undoubtedly precedes the passage of the discharge; and it is possible that this preliminary ionization may render the molecules more reactive than usual towards each other. It is known that the exposure of some gaseous mixtures to a source of intense ionization causes their combination at quite low temperatures. The point of controversy would, therefore, appear to be whether in the ignition of gaseous mixtures by an electric spark ionic rather than thermal phenomena predominate; whether, in fact, an electric spark is more effective as an ionizer than is a flame or a heated solid.

Insufficient experimental work has been done to enable a decision to be reached on this matter. The character of the phenomena of spark ignition seems to differ from that of the phenomena of ignition by the prolonged contact of a heated surface. Thus, the type of curve that can be constructed connecting 'igniting-current' or 'spark-energy' with percentage composition of mixtures of any given inflammable gas with air differs from the type of curve connecting ignition temperatures, as determined by the first method described, with percentage composition (*see* Fig. 1). It may be, however, that this difference is due to a large extent, if not entirely, to the short duration and small size of the electric spark; also that the rapidity with which flame can travel in a mixture away from the source of heat becomes of importance equally with the susceptibility of the mixture to ignition when the source of ignition is very small and lasts but a short time. It may be noted that the spark ignition curve in Fig. 1 is nearly the inverse of the speed-percentage curve for flame in methane-air mixtures described in the ensuing section of this article (*see* Fig. 2).

Limits of Inflammability.—If the whole volume of a gaseous mixture be raised to its ignition-temperature, as it is, for example, in the cylinder of a Diesel engine, it necessarily follows that the whole of it is inflamed. On the other hand, the introduction into a gaseous mixture of a small source of heat at a tempera-

ture considerably higher than the ignition-temperature of the mixture need not cause complete propagation of flame.

It is well known that when a flame is introduced into a mixture of an inflammable gas and air containing but little inflammable gas, a 'cap' or aureole is formed around the flame; and that this cap is larger the greater the proportion of inflammable gas present. The coalminer regularly uses this formation of a cap as an indication of the presence of firedamp in the workings of the mine. It has been observed also that in a current of gas and air, poor in combustible gas, passing a lamp flame or similar source of heat, the cap or aureole may become separated from the burning body by which it is originated and be carried along for a limited distance, giving a 'cloud' of flame. But unless this cloud were fed by some mixture richer in combustible gas than that in which it originated it would gradually die away. In a uniform mixture of gas and air the flame could only be carried on automatically through-out the extent of the mixture if the inflammable gas were present in quantity above what is termed the 'lower limit' of inflammability.

When a source of heat is introduced into a stagnant mixture of combustible gas and air, two things are necessary to ensure propagation of flame throughout that mixture, namely, (a) an adequate means of ignition, and (b) a sufficient proportion of inflammable gas.

Supposing that too small a proportion of combustible gas is present, only a small quantity of heat per unit volume of mixture is generated when the layer surrounding the initial source of heat is inflamed, and the products of combustion have to impart heat to a considerable volume of inert gases. The number of collisions between molecules of combustible gas and of oxygen that are chemically effective is therefore small. Such collisions, resulting in combination, will occur only in the neighbourhood of the initial source of heat around which an aureole will form of a size dependent on the nature and quantity of the combustible gas present.

As the proportion of combustible gas is increased a proportionately greater quantity of heat is evolved per unit volume of mixture, and a smaller quantity of inert gases is present to absorb it. At length a point is reached when the amount of heat contained in the products of combustion of any given layer is just sufficient to raise the adjacent layer to its ignition temperature. Flame is then propagated progressively throughout the mixture without any necessity for the continued presence of the source of heat which started the inflammation, and the mixture is said to 'inflame' or 'explode,' according to the rapidity of the propagation.

To ensure propagation of flame throughout the mixture, therefore, it is necessary for the initial source of heat to be of a volume, intensity, and duration sufficient to raise the layer of gases surrounding it to the ignition temperature of the mixture, and for the heat contained in the products of combustion of this first layer to be sufficient to raise the next layer to its ignition temperature, and so on. An inflammable mixture can be defined as a mixture in which flame can spread to any distance, independently of, and away from, the original source of ignition

In the case of mixtures of any particular combustible gas with air (or oxygen) there are, under given physical conditions, certain limits of composition within (but not outside of), which self-propagation of flame will take place after ignition has once been effected. These limits, defined in terms of the percentage of the combustible gas present, are usually referred to as the 'lower' and 'higher' limits of inflammability of the gas under the given conditions. For any particular gas they differ slightly with the position of the source of ignition, since the progress of the flame may be assisted or retarded by convection-currents dependent upon whether it has to pass in an upward or downward direction. For example, with mixtures of methane and air and of acetone vapour and air the limits, expressed as percentages by volume of the mixtures, are as follows for upward, downward, and horizontal propagation of flame:—

Lower limit

	Upward	Downward	Horizontal
Methane	5·40	6·00	5·40
Acetone vapour	2·15	2·35	2·20

Higher Limit

	Upward	Downward	Horizontal
Methane	14·80	13·40	14 30
Acetone vapour	9·70	8·50	9·50

The limits of inflammability of a number of gases and vapours, mixed with air at atmospheric temperature and pressure, are given in the table that follows. For all but hydrogen and carbon monoxide the criterion of inflammability adopted for the determinations was propagation of flame throughout a 2½-litre sphere, ignition being at the centre. The figures for hydrogen and carbon monoxide refer to upward propagation of flame.

Gas	Lower limit p.c.	Upper limit p.c.
Hydrogen	4·1	71·5
Carbon monoxide	12·5	73·0
Methane	5·6	14·8
Ethane	3·1	10·7
Propane	2·2	7·4
Butane	1·7	5·7
Pentane	1·4	4·5
Ethylene	3·0	22·0
Acetylene	3·3	52·3

Vapour	Lower limit p.c.	Upper limit p.c.
Benzene	1·5	5·6
Toluene	1·4	5·4
Ethyl alcohol	4·4	—
Methyl alcohol	6·5	24·0
Ethyl ether	2·0	5·0
Acetone	2·25	9·6
Carbon disulphide	4·2	—
Petroleum benzine	1·1	3·8
Gasoline	1·5	7·3

The Effect of Temperature.—From what has been said in the preceding paragraph, it is evident that the self-propagation of flame through a mixture is, in principle, dependent on the temperature that the portion of the mixture which is burning can impart to the portion which is about to burn, from which it follows that the higher the initial temperature of the mixture the less dependent is the propagation of flame upon the heat generated by combustion. Hence the effect of increasing the initial temperature of mixtures of an inflammable gas and air should be to widen the range of inflammability, lowering the lower, and raising the higher limit.

Thus it has been found experimentally that a progressive increase in the initial temperature of mixtures of methane and air from 20° to 700° caused a corresponding decrease in the amount of methane required to enable self-propagation of flame to take place from 6·00 to 3·25 p.c. (downward propagation). Similarly, the higher limit was raised gradually from 13·40 p.c. at 20° to 16·40 at 600°.

The Effect of Pressure.—As exemplifying the influence of the initial pressure of gaseous mixtures upon their limits of inflammability, the case of mixtures of methane and air may be cited. A reduction of the initial pressure, at 20°C., from 760 to 380 mm. has but little effect on the limits; but below a pressure of 300 mm. mercury the effect is marked, the limits narrowing rapidly until, at a pressure of 120 mm. no mixture of methane and air is capable of self-propagation of flame (downwards). On the other hand, an increase of pressure above 760 mm. slightly raises both the lower and the higher limit, the figures at 6 atmospheres being 6·40 and 14·05 p.c. of methane respectively, for downward propagation of flame.

The lower limit with mixtures of hydrogen and air, and of carbon monoxide and air, is also raised by increasing the initial pressure above 760 mm., but with these two gases the higher limit is lowered.

Mixtures of Inflammable Gases.—In the case of a mixture of inflammable gases such as coal gas, a general formula is available by means of which its limits of inflammability with air may be calculated if its composition, and the corresponding limits of the individual gases are known. If a, b, c, . . . are the relative proportions of its components, and A, B, C, . . . their respective limits of inflammability, then L, the limit for the mixed gases, is given by the equation:—

$$L = \frac{a+b+c+ \cdots}{\dfrac{a}{A}+\dfrac{b}{B}+\dfrac{c}{C}+ \cdots} \quad . \quad . \quad \text{(i.)}$$

This relationship holds both at the lower and the higher limit. It implies that if a limit-mixture with air of one inflammable gas is mixed in any proportion with a limit-mixture with air of another inflammable gas, a limit-mixture results.

It has been necessary to emphasize the fact that this formula refers to mixtures of combustible gases with air, for the reason that the presence of any considerable quantity of an uninflammable constituent, such as nitrogen, in the commercial gas would narrow the range of inflammability, just as the range for a pure gas is narrowed if the oxygen-content of the air is reduced.

The effect of Incombustible Gases.—The effect of a reduced oxygen-content of the 'air,' or of the presence of inert constituents in the 'combustible gas,' is more marked at the higher than at the lower limit. This is well illustrated

by determinations of the limits for mixtures of methane with 'atmospheres' containing different proportions of oxygen. These determinations afford an index of the general effect of 'inert' gases on the limits of inflammable gases in general when the actual data are not available; the effect of carbon dioxide is rather more pronounced than that of nitrogen.

Atmosphere		Methane—p.c.	
Oxygen	Nitrogen	Lower limit	Higher limit
20·90	79 10 (air)	5·60	14·82
19·22	80·78	—	12·93
18·30	81·70	—	11·91
17·00	85·00	5·80	10·55
15·82	84·18	5·83	8·96
14·86	85·14	6 15	8·36
13·90	86·10	6 35	7·26
13·45	86·55	6 50	6·70
13·25	86·75	No mixture capable of propagating flame.	

Speed of Propagation of Flame.—During the propagation of flame in any 'limit' mixture, a balance is struck between heat generated by combustion and heat employed in starting combustion, together with heat lost by conduction and radiation. Theoretically, therefore, provided that the amount of energy imparted to the system by the initial source of ignition is small, so that no appreciable impetus to the propagation of flame occurs near the source of ignition, flame should travel in a limit-mixture at a uniform speed This is found to be so in practice; the speed of the flame is slower in a limit mixture for downward than in one for upward propagation; but under either condition it is quite uniform throughout the extent of the mixture.

It is otherwise when the proportion of inflammable gas lies at some intermediate point between the limits; that is to say, when the mixture is such that one layer on burning is capable of imparting to it a temperature higher than the ignition-temperature of the mixture. The phenomena of propagation of flame in such mixtures are dependent in a marked degree upon the conditions under which ignition is effected, so that it is necessary when speaking of the propagation of flame through them to specify exactly those conditions.

When ignition of a mixture of combustible gas and air has been effected at the open end of a long tube which is closed at the other end, the flame can be propagated in two principal ways, namely, (a) by transmission (by radiation, conduction, and convection) of the heat developed by the burning of one layer of gas to the layer adjacent to it; and (b) by the transmission of a sufficiently high pressure.

According to the first mode of propagation, the flame travels along the tube at a uniform speed for a certain distance, and then develops vibrations, swinging backward and forward with oscillations of increasing amplitude. The mean speed of the flame during this vibratory movement, which comprises a series of compression and rarefaction waves, is usually greater than the speed of the uniform movement. According to the nature of the mixture, either the vibrations may continue to the end of the tube, or the flame may become extinguished

during a particularly violent vibration (e.g. during rarefaction). Or again, a sudden permanently greater enhanced speed of flame may be developed as the result of the second mode of propagation coming into play (during a compression).

During this second mode of propagation each layer of gas is compressed so suddenly that it is raised beyond its ignition temperature by the heat of compression, and in burning it compresses in turn the unburnt layer in front of it. As already stated, the speed of the flame during this mode of propagation is permanently enhanced; it is, in fact, the maximum speed attainable by the flame and is a physical constant for each mixture of gases. The phenomenon is termed the 'detonation wave.'

When ignition takes place at the closed end of a tube open at the other end, the flame travels at a rapidly increasing speed towards the open end. If the tube is long enough, the flame may eventually assume a vibratory character and the detonation-wave may be developed.

What has been said in this short summary refers only to mixtures of a combustible gas with air; mixtures with pure oxygen behave somewhat differently. With regard to the latter, it may be stated that, in general, (a) the preliminary period of uniform movement is shorter, (b) a rapid acceleration follows, and (c) this is immediately succeeded by the detonation-wave without any vibratory movement taking place.

Of the different phases in the propagation of flame in mixtures of gases, the two regarding which most information is available are the 'uniform movement' and the 'detonation wave.' Some further account of these will now be given.

The Uniform Movement.—The initial slow propagation of flame that takes place when an inflammable mixture at rest is ignited at a point, is usually regarded as controlled by the transference, by conduction, of the heat developed by the combustion of the mixture immediately surrounding the point of ignition, whereby successive contiguous portions of the mixture are raised in temperature until chemical action becomes rapid. The initial speed of propagation of flame in a given mixture away from the point of ignition should mainly depend, according to this view (a) on the conductivity for heat of the unburnt mixture, and (b) on the velocity with which a moderately heated layer begins to react chemically and so to rise gradually in temperature; or, in other words, on the rate of change of reaction velocity with temperature.

Under certain conditions, with all inflammable mixtures of gases and air at atmospheric temperature and pressure, the initial slow propagation of flame can be maintained at a uniform speed over a considerable distance of travel from the point of ignition. The conditions most favourable, or perhaps even necessary, to initiate and maintain this 'uniform movement' of flame are (a) that the inflammable mixture should be contained in a long straight tube open at one end and closed at the other; and (b) that ignition should be at the open end by a source of heat not greatly exceeding in temperature the ignition temperature of the mixture, and not productive of mechanical disturbance of the mixture. The speed of the uniform movement

then depends on the composition of the mixture (presumed to be at atmospheric temperature and pressure), and on the diameter of the tube in which it is contained.
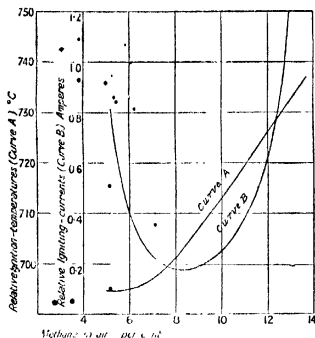
With a tube of a given diameter the speed

Fig. 1.

of the uniform movement of flame in a mixture can be regarded as a definite physical constant for that mixture, and its measurement is of considerable value in enabling a judgment to be formed of the behaviour of the mixture under normal conditions of burning.
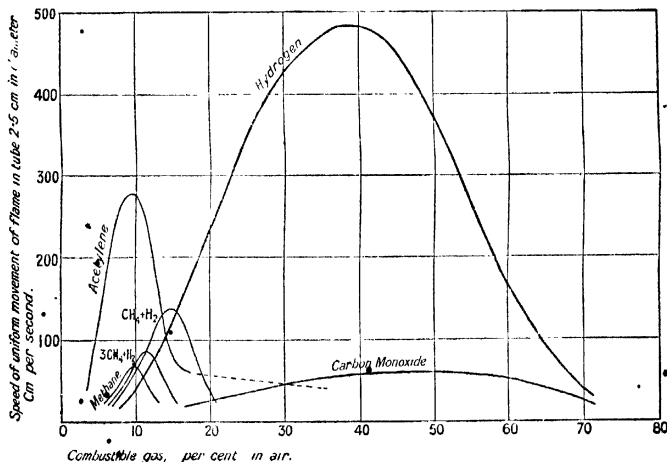
In Fig. 2 are shown speed-percentage curves for the uniform movement of flame in mixtures of some of the common combustible gases with air over the whole range of inflammability for each gas. All the measurements were made in a tube of 2·5 cm. internal diameter, so that they are strictly comparable one with another. Apart from the striking differences in the speeds obtainable in different gases displayed by this diagram, a noticeable feature of the curves is the fact that with each gas the maximum speed is obtained not, as might perhaps be expected, with the theoretical mixture for complete combustion, but over a range of mixtures containing an excess of inflammable gas.

The extent to which the speed of the uniform movement is affected by the size of the tube along which the flame travels has been determined for mixtures of methane and air. The results are recorded in Fig. 3. For all practical purposes it can be assumed that the speed of the uniform movement of flame in mixtures with air of gases other than methane will be affected to a similar degree, so that the absolute speeds of the flames in pipes 30, 60, and 90 cm. in diameter will be respectively about 2·5, 3, and 3·5 times as great as the speeds recorded in the 2·5 cm. tube (Fig. 2).

It should be noted that the uniform speeds of the flames in tubes of large diameter (greater than 10 cm. for methane-air mixtures) are not, strictly speaking, those of the ' uniform movement ' as previously defined, since they are not controlled solely by conduction of heat. A

Fig. 2.

second factor, namely, convection, comes into play when the tubes are large, and is responsible for the enhanced speed of flame.

Mixtures of Inflammable Gases.—It has been found that a similar expression to that used for calculating the limits of inflammability of mixed combustible gases can be employed to determine, with fair accuracy, the maximum speed of

uniform movement of flame for any complex gas mixed with air, from a knowledge of its composition and the maximum speeds of each of the components. The expression is :—

$$c = \frac{a+b+c+\cdots}{\dfrac{a}{S_a}+\dfrac{b}{S_b}+\dfrac{c}{S_c}+\cdots} \qquad \text{(ii.)}$$

in which S is the speed required; a, b, c . . . the proportions of the different simple constituents in the complex inflammable gas (coal-gas, for example); and S_a, S_b, S_c . . . the maximum speeds of flame in mixtures of the individuals with air.

Formula (i.) can be used also for determining the composition of the mixture of the complex
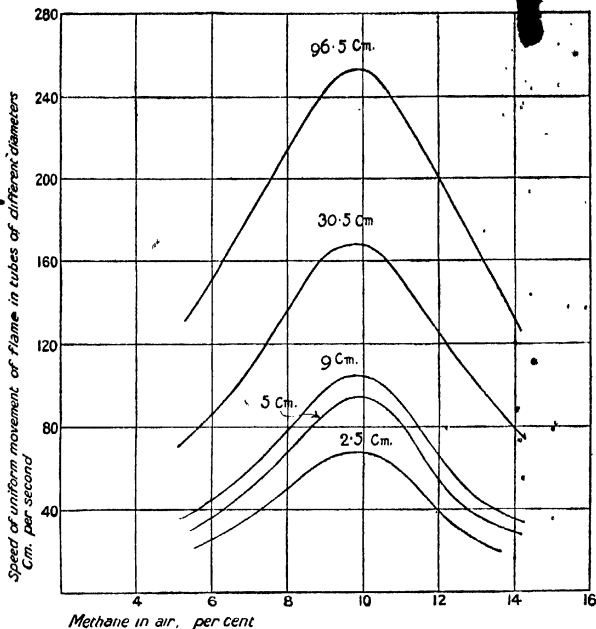

FIG. 3.

Methane in air, per cent

gas and air in which the speed of the uniform movement of flame will be greatest; and formula (ii.) for determining the speed of flame in the limit-mixtures, and (though with rather less accuracy) in the mixture containing the gases in theoretical proportions for complete combustion.

The value of these formulæ will be appreciated if reference be made to Fig. 2, wherein are recorded, for comparison with the simple gas-air mixtures, the speeds of the uniform movement of flame in mixtures of the composite gases $CH_4 + H_2$ and $3CH_4 + H_2$ with air as determined by actual measurement in a tube 2·5 cm. in diameter. It will be seen that the gas with the lower speed of flame and the smaller range of inflammability (methane) has the predominating influence in deciding the magnitude of these constants for the mixed gas

The Effect of Incombustible Gases.—In addition to restricting the limits of inflammability, the presence of an incombustible gas mixed with the combustible gas has the effect of reducing the speed of flame in any of the mixtures with air. This effect is illustrated in Fig. 4, which shows the speed-percentage

curves for the uniform movement of flame in mixtures of methane with nitrogen-oxygen mixtures containing less oxygen than air, the
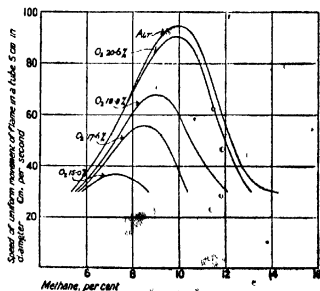

Methane, per cent   FIG. 4.

curve for air-mixtures being given for comparison. This diagram shows also the effect of nitrogen in reducing the range of inflammability and establishes the fact, theoretically

deduci... ... the speed of travel of flame is the same ... ... limit-mixtures that comprise the same constituent gases. The experiments from which these curves are constructed were made in a tube 5 cm. in diameter, so that the speeds are not directly comparable with those recorded in Fig. 2.

B.—THE DEVELOPMENT OF 'DETONATION' IN GASEOUS EXPLOSIONS. THE EXPLOSIVE WAVE AND 'RETONATION'—RATIO OF EXPLOSION

It was in the year 1881 that Berthelot and Vieille, and independently also Mallard and Le Chatelier, announced the discovery of the rapid acceleration of the initial velocity of inflammation in the progress of gaseous explosions and the final attainment of the enormously higher constant velocity of the 'explosion wave.' Since that date, the phenomena associated with the development of 'detonation' and the propagation of the explosion wave has been extensively studied in this country by H. B Dixon and his co-workers.

Mallard and Le Chatelier devised a photographic method for investigating the initial phases of gaseous explosion, which consisted in recording on a sentitised plate, moving at a known velocity on a vertical plane, the movement of the flame as it travelled along a horizontal glass tube. A graph compounded of the two velocities was thus obtained.

H. B. Dixon's experimental method consisted in photographing the explosion flame travelling along a horizontal tube on a highly sensitive film rotated vertically with a constant high velocity (varying, however, between twenty-five and fifty metres per second in different experiments), the explosion tube being placed at such a distance from the camera that the size of the image was about one-thirtieth that of the flame. In this way it was found possible to analyse the progress of an explosion from its point of origin up to the final attainment of its maximum force and velocity in 'detonation.' The investigation also included the discovery of the wave of 'retonation,' which is thrown back through the still burning gases from the point where detonation starts (a phenomenon also discovered by Le Chatelier independently in 1900), of the effects of collision between two explosion waves, and of the passage of reflected waves through the hot products of explosion.

The phenomena associated with the development of an explosion in a gaseous mixture, fired in a closed tube by a spark passed between wires a few inches from the closed end, are very clearly shown in the photograph reproduced in Fig. 5 which is analysed in Fig. 6. This photograph was taken during an experiment in which carbon disulphide was exploded with a quantity of oxygen represented by the expression CS_2+5O_2. The flame in starting at the point o, sends out

invisible compression waves in both directions along the tube, which travel in advance of the flame with the velocity of sound through the unburnt gases, as represented by the dotted lines OM, ON in the diagram. The flame itself, travelling at first more slowly than the compression waves, traces the curves OA and OB. The compression wave ON, on reaching the closed end of the tube, is reflected back again as NC, and, on meeting the flame (which is still travelling in the direction OA), retards it, and passes thence through the hot and probably still burning gases as the visible wave CD. An instant later it overtakes at D the front of the flame, travelling in the direction OB, thereby accelerating it and increasing its luminosity in
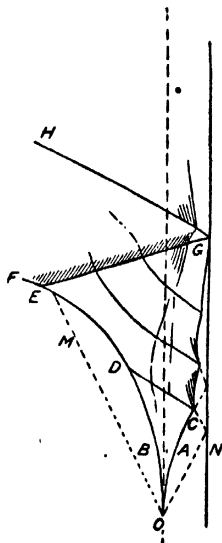

FIG. 5.   FIG. 6.

consequence of the quickened combustion. The flame then continues to move forward with rapidly accelerated velocity until 'detonation' is set up at the point E. At this point a strongly luminous wave of compression EG (the "retonation wave') is sent backwards through the still burning gases, which, on reaching the near end of the tube, is reflected back again as GH. The detonation 'wave' EF passes onward through the mixture with its characteristic uniform high velocity and intense luminosity. Fig. 7 is a similar photograph showing the development of 'detonation,' and the phenomenon of 'retonation' in the case of mixture of cyanogen and oxygen $(C_2N_2+O_2)$ fired near the closed end of a tube.

Except in special circumstances (e.g. when it is reinforced by another reflected wave) the velocity of the retonation wave is always

inferior to that of detonation; thus Le Chatelier gives 2990 metres per second for the 'detonation wave' and 2330 metres per second for the 'retonation wave' in an equimolecular mixture of acetylene and oxygen. When, however, the 'retonation wave' is developed just at the closed end of a tube (e.g. when the explosive mixture is fired at such a distance from the closed end that 'detonation' is set up just as the flame arrives at the end) it may be reinforced by a reflected wave, in which case its velocity cannot be distinguished from that of a true 'detonation.'

The explanation of the intense luminosity of the retonation wave, and its higher velocity than sound through the exploded gases, is to be found in the fact that the combustion during the initial stages of an explosion is very much slower than when detonation has been set up. Under the extreme conditions of 'detonation' the temperature of each successive layer of the explosive mixture is suddenly raised to the ignition point by adiabatic compression, and it is probable that a large proportion of collisions between chemically opposite molecules are fruitful of change. The whole combustion is probably completed in an immeasurably short interval of time, as the result of a comparatively limited number of successive molecular collisions. But during the initial period of the explosion ('inflammation') not only is the flame propagated with a much slower ve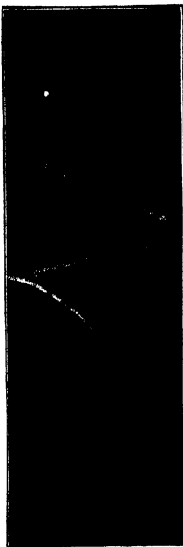locity, but also the actual process of combustion is much more prolonged than in detonation, and at the moment when detonation is set up combustion is still proceeding in the layers of gas for some distance behind the flame-front. The 'retonation' wave, in passing backward through these layers, quickens this residual combustion, and is itself thereby rendered highly luminous. This interpretation is supported by the repeated observations of Dixon, that the collision of two flames, in neither of which 'detonation' has been determined, will frequently give rise to reflected waves more rapid and more luminous than the incident waves. There can be little doubt as to the important part played by reflected-waves in determining the violent shattering effects associated with gaseous explosions on a large scale.

The Explosion Wave.—Berthelot and Vieille, in announcing their discovery of the develop-

FIG. 7.

ment of detonation '(l'onde explosive')' in gaseous explosions, described it as 'une certaine surface régulaire, où se développe la transformation, et qui réalise un même état de combinaison, de température, de pressure, etc. Cette surface, une fois produite, se propage ensuite, de couche en couche, dans la masse tout entière, par suite de la transmission des chocs successifs des molécules gazeuses amenées à un état vibratoire plus intense en raison de la chaleur dégagée dans leur combinaison, et transformées sur place, ou, plus exactement, avec un faible déplacement relati, . . .' Such conditions are comparable with those of a sound wave passing through the gaseous mixture, with, however, the important difference that, whereas a sound wave is propagated from layer to layer with a small compression and a velocity determined solely by the physical condition of the vibrating medium, it is an abrupt change in chemical condition which is propagated in the explosion wave, and which generates an enormous force as it passes through each successive layer of the medium.

In their experimental work Berthelot and Vieille proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and of the material or diameter of the tube employed (at least above a certain small limiting diameter). It is also immaterial whether the tube is laid out straight, coiled round a drum, or even zigzagged. They also concluded that the velocity is independent of the initial pressure, but this is not strictly correct, as H. B. Dixon has since shown. The rate increases slightly with the initial pressure, attaining a nearly constant value at a pressure of about two atmospheres.

It must be understood that when detonation is once determined in a particular explosive mixture, the wave is propagated with constant velocity (i.e. for a given initial temperature and pressure), which velocity is indeed an important physical constant for the particular mixture. The following 'rates of explosion,' as determined by Dixon, may be considered as typical of the extremely high velocities attained:—

RATES OF EXPLOSION FOR MIXTURES FIRED AT 10° AND 760 MM.

Mixture	Metres per second
$2H_2+O_2$	2820
H_2+Cl_2	1729
$2CO+O_2$ (moist, sat'd at 28)	1703
NH_3+3O_2	2390
CH_4+2O_2	2322

In detonation, each successive layer of the explosive mixture is fired by compression, and the chemical change in the wave occurs under strictly adiabatic conditions. This means that the chemical action is more intense and of much shorter duration than during the initial phases of an explosion ('inflammation'); moreover, the pressures developed in the wave and the consequent shattering effects are much greater than in ordinary explosions. Thus, for example, in a mixture $2H_2+O_2$, fired at the ordinary atmospheric temperature and pressure, the initial velocity of the flame (i.e. during the short period of 'inflammation') is only 20 metres per second, and chemical action endures in each successive layer of the mixture for as long as

one-twentieth of a second. As soon, however, as detonation is set up, the flame travels forward with a constant velocity of 2820 metres per second, and the duration of chemical action in each successive layer certainly does not exceed $\frac{1}{50000}$ and possibly not much less than $\frac{1}{10000}$ of a second. Needless to say 'detonation' is not set up in a gas-engine cylinder; the terrific force developed in detonation would play havoc with the mechanism.

Dixon's photographic researches, already alluded to, have demonstrated beyond doubt the important *rôle* of 'compression waves' in determining detonation in explosive mixtures, and it is probable that the disastrous effect of colliery explosions are primarily due to the intensifying effects of reflected compression waves upon the burning mixture of gas and (or) coal dust and air.

In 1899 D. L. Chapman published a mathematical analysis of the explosion wave. Discarding Berthelot's sound-wave theory, which indeed had led to values for rates of explosion which were difficult to reconcile with facts, he regards the explosion wave as a wave of compression not in a homogeneous medium, but in a medium which is discontinuous in the vicinity of the wave-front. It is assumed (1) that the 'front' of the wave (i.e. from the unexploded gas to the point of maximum pressure) does not alter in character, or, in other words, that every portion of the wave travels with the same velocity; (2) that the velocity is the minimum consistent with (1); and (3) that at the point of maximum pressure the chemical change concerned in the propagation of the wave is complete. The unburnt gases immediately in

front of the wave are, of course, fired by compression, and the abrupt variation in the density and pressure of the medium is due to the chemical change. Chapman's formula for the velocity of the explosion wave in centimetres per second is—

$$V = \frac{2RJ}{\mu C_v{}^2}\left[\left\{(m-n)C_p + mC_v\right\}C_p t_0 + (C_p + C_v)h\right]$$

when R=the gas constant (1·985), J=the dynamical equivalent of heat (42+10⁶ ergs.), μ=the gram equivalents of the mixture exploded, n and m = the number of gaseous molecules before and after the chemical change in the wave, C_p and C_v=the mean specific heats of the products at constant pressure and volume respectively, h=the total heat generated in the wave, and t_0=the initial temperature (abs.) of the mixture exploded.

From the fact that the dilution of electrolytic gas $(2H_2+O_2)$ with oxygen lowers its rate of explosion a little more than a corresponding dilution with nitrogen, Chapman considers it improbable that there is any appreciable dissociation of steam in the wave. He assumes that the molecular heat of steam rises more rapidly with temperature than that of a diatomic gas, and that the molecular heats of oxygen, hydrogen, nitrogen, and carbon monoxide may for all practical purposes be considered as equal at any given temperature. Selecting some seventeen of Dixon's found rates of explosion, he has calculated by means of his formula the corresponding molecular heats and temperatures, arriving at the following results for Cv at intermediate temperatures by interpolation :—

Temperature	4300°	4000°	3700°	3400°	3100°	2800°	2500°
Cv steam	14·750	14·297	13·750	13·102	12·250	11·040	9·797
Diatomic gases	7·707	7·674	7·641	7·608	7·575	7·542	7·509

With the aid of this series of numbers he proceeded to apply his formula to the calculations of the rates of explosions of some forty other mixtures investigated by Dixon, finding in all cases close agreement between the found and calculated values, of which the following may suffice as examples :—

Mixture exploded	Products in the wave	Temp.	Rate of explosion Metres per sec.	
			Calculated	Found
$2H_2+2N_2O$	$2H_2O+2N_2$	3813°	2408	2305
$4H_2+2N_2O$	$2H_2O+2N_2+2H_2$	3077	2604	2545
$6H_2+2N_2O$	$2H_2O+2N_2+4H_2$	2612	2720	2705
$2H_2+2N_2O+2N_2$	$2H_2O+4N_2$	3077	2097	1991
$C_2H_4+2O_2$	$2CO+2H_2O$	4365	2619	2581
$C_2H_4+3O_2$	$2CO+2H_2O+O_2$	3882	2348	2368
$C_2H_2+O_2$	$2CO+H_2$	5029	3101	2961
CH_4+O_2	$CO+H_2O+H_2$	2772	2502	2528
$2CH_4+3O_2$	$2CO+4H_2O$	3764	2485	2470
$2CH_4+3O_2+N_2$	$2CO+4H_2O+N_2$	3513	2353	2349

A characteristic feature of detonation is the extremely short duration of chemical action and the subsequent rapid cooling of the products, as compared with ordinary combustion. Some

years ago, W. A. Bone and B. Lean found by a photographic method that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas is certainly less than $\frac{1}{1000}$ second, a much shorter interval of time than was required to shatter a tube of thin glass attached to the end of the explosion coil used. This tube, although invariably smashed by the force of the explosion, always appeared perfectly intact in the photograph. Dixon's subsequent photographic researches have demonstrated the abrupt suddenness with which the gases attain the maximum temperature in detonation, the intensity and short duration of luminosity, and the subsequent rapid cooling of steam in the wave, for, despite the instantaneous cooling of the products, there is less than 1 per cent. of the gases left uncombined after the wave has passed through electrolytic gas $(2H_2+O_2)$.

Influence of an Excess of an Inert Gas upon the Rate of Explosion of a particular Mixture.— It has been found experimentally that whereas an excess of nitrogen or oxygen retards the rate of explosion of a particular mixture, an excess of hydrogen actually increases it. Thus in the case of electrolytic gas, we have—

Mixture exploded				Rate metres per sec.
$2H_2 + O_2$	.	.	.	2817
$2H_2 + O_2 + 2H_2$	.	.	.	3268
$2H_2 + O_2 + 4H_2$	.	.	.	3527
$2H_2 + O_2 + 6H_2$	.	.	.	3532
$2H_2 + O_2 + O_2$	.	.	.	2328
$2H_2 + O_2 + 3O_2$	.	.	.	1927
$2H_2 + O_2 + N_2$	.	.	.	2426
$2H_2 + O_2 + 3N_2$	.	.	.	2055

The accelerating influence of an excess of hydrogen was for long an enigma, but it was perfectly explained when Chapman published his formula. It must, however, be understood that an excess of oxygen always has a somewhat greater influence than a corresponding excess of nitrogen by virtue of its relatively higher density

The Burning of Gaseous Carbon.- Of the many important facts brought to light during the course of Dixon's investigations none are of greater interest than those relating to the burning of gaseous carbon in the explosion wave, as illustrated by the case of cyanogen. In view of the fact that the molecular heat of combustion of cyanogen, when burnt completely to carbon dioxide, is 259·6 K.C.Us , whereas, if burnt to the monoxide, it would only be 123 K C Us., it might be expected that the rate of explosion for a mixture $C_2N_2 + 2O_2$ would be much higher than for $C_2N_2 + O_2$, if gaseous carbon is primarily burnt to carbon dioxide in the wave The exact opposite is the case, however, as the following results show —

Mixture	Products	Rate	
$C_2N_2 + O_2$	$2CO + N_2$	2728	metres per sec.
$C_2N_2 + 2O_2$	$2CO_2 + N_2$	2321	

Still more cogent is the evidence in favour of the initial formation of carbon monoxide in the wave, when the following figures are considered :—

	$C_2N_2 + O_2$	$C_2N_2 + O_2 + N_2$	$C_2N_2 + O_2 + O_2$
Rate	2728	2398	2321

The conclusion to be drawn from the preceding figures is that cyanogen is initially burnt to carbon monoxide and nitrogen in the wave itself, any excess of oxygen afterwards burning up the carbon monoxide as the gases cool down in the rear of the wave.

This conclusion was driven home by Dixon, in conjunction with Strange and Graham, by photographing on a sensitive film rotated at a speed of about 1500 metres per minute, the explosion flame in the case of the three mixtures (a) $C_2N_2 + O_2$, (b) $C_2N_2 + O_2 + N_2$, and (c) $C_2N_2 + 2O_2$. In each case the flame was photographed, after detonation had been set up, as it dashed past a glass window inserted into the lead explosion coil [2] The image obtained in the case of (a) showed an intensely brilliant flame (the explosion wave), slightly drawn out in tapering form ; in the case of (b), with nitrogen as diluent, the flame was less brilliant and somewhat more drawn out than in (a) but with (c) the flame, whilst no more luminous than in (b), was drawn out to great length, owing to the continued combustion of carbon monoxide in the rear of the wave The following diagram, Fig. 8 (approximately to scale), will convey an idea of the relative durations of the flames in the three cases :—
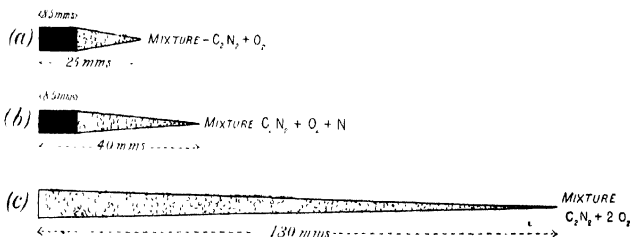

FIG. 8.

The Burning of Hydrocarbons in the Wave.— It was during the course of measurements of the rates of explosion of hydrocarbons with varying proportions of oxygen in 1891–92 that Dixon and his collaborators rediscovered facts (originally set forth by Dalton in his ' New System of Chemical Philosophy ') which finally disposed of the dogma that in a deficient supply of oxygen a ' selective ' burning of hydrogen occurs. Bone, in conjunction with Lean and Cain, found that when either ethylene or acetylene is detonated with its own volume of oxygen the ultimate products consist almost entirely of carbon monoxide and hydrogen.[1] The rates of explosion of hydrocarbon-oxygen mixtures, whilst they do not reveal the real mechanism of the combustion, show very clearly that,

as in the case of cyanogen, the carbon of a hydrocarbon is burnt to, the monoxide in the wave itself, the formation of the dioxide being an after-effect and taking place in the rear of the wave. In the cases of methane and acetylene the fastest rates are observed with equimolecular mixtures, whereas with ethylene the rate increases with the proportion of oxygen up to the limit $C_2H_4 + 2O_2$.

C.—THE PRESSURES PRODUCED IN GASEOUS EXPLOSIONS.

Many investigators, from the time of Bunsen's well-known experiments in 1867 onwards, have measured the pressures produced in gaseous explosions, with doubtless considerable success so far as what may be termed the mean effective

[1] *Vide* Lean and Bone, Trans. Chem. Soc. 1892, 61, 873, and Bone and Cain, *ibid.* 1897, 71, 26.

[2] Trans. Chem. Soc. 1896, 69, 759.

pressures are concerned. The explosion vessel employed by Bunsen was a stout glass tube 8·15 cm. long, 1·7 cm. internal diameter, and of 18 cc. capacity. It was closed by a suitable valve, the load on which could be adjusted until it was just lifted when the explosive mixture was fired by means of a powerful spark passed along the axis of the tube. Bunsen considered that the combustion would occur under adiabatic and 'constant volume' conditions, and he identified the rate of ignition of a particular mixture with that of the completion of chemical change. In calculating from his results the corresponding flame temperatures, he assumed the constancy of the specific heats of steam and carbon dioxide. Finding that the pressures recorded in the cases of electrolytic gas and of a mixture of carbon monoxide and oxygen in their combining proportions (namely, 9·5 and 10·1 atmospheres respectively) were somewhat less than one-half of those theoretically re-

quired on the above assumption, he concluded that in each case combustion had proceeded *per saltum*, owing to the supposed theoretical flame temperatures exceeding the limits at which steam and carbon dioxide respectively are completely dissociated. The problem was again attacked independently by Mallard and Le Chatelier in 1883,[1] and by Berthelot and Vieille in 1885.[2] The last-named fired various gaseous mixtures at atmospheric pressure in a spherical iron bomb, measuring the effective pressures by the movement of a light piston working against a spring in a tube attached to the bomb. In order to gain some information respecting the possible cooling influence of the walls upon the effective pressures recorded, three bombs of different capacities, namely, A. of 300 cc. B. of 1500 cc., and C. of 4000 cc, were employed. The results, expressed in each case as atmospheres in excess of the atmospheric pressure, were as follows :—

Bomb	A	B	C
Capacity in cm.³	300	1500	4000
Surface in cm.²	216	648	1200
Surface per unit volume	0·72	0·43	0·33
Diameter in cm.	6·0	14·2	21·7
Length of firing piece in cm.	6·3	5·3	6·3
Travel of flame before reaching the piston in cm.	9·1	16·3	24·8
	Atms.	Atms.	Atms.
Mixture exploded $2H_2+O_2$	7·41	9·69	9·80
$2CO+O_2$	9·29	9·93	10·21
CH_4+2O_2	13·94	14·81	16·31
$C_2N_2+O_2$	—	—	25·11
$C_2N_2+2O_2$	—	—	20·96
Time required for flame to travel from the firing piece to piston of indicator.			
Mixture $2H_2+O_2$	0·00104 sec.	—	0·00214 sec.
$2CO+O_2$	0·01286 sec.	—	0·01551 sec.

Perhaps the most notable feature about these results is the smallness of the difference between the pressures observed with bombs A and C in any particular case. These differences might at first sight be attributed to the (supposed) much smaller cooling influence of the walls of the bomb C as compared with bomb A, but if this were the true explanation the difference should be greater with the slow-burning $2CO+O_2$ mixture than with the fast-burning $2H_2+O_2$, whereas the opposite was the case. Moreover the fact that dilution of the mixture $2H_2+O_2$ with twice its own volume of nitrogen almost obliterated the difference between the pressures observed in the cases of bombs A and C (the ratio $\frac{pC}{pA}$ for the diluted being 0·95, as against 0·76 for the undiluted mixture) is all against the cooling theory. The more probable explanation is to be found in the fact that, owing to the much longer travel of the flame before it reached the piston of the indicator in bomb C as compared with A, the explosion would be in a more advanced phase of its development, and this would be most marked in the case of the fastest burning mixtures. Berthelot and Vieille assumed

that in the above experiments completion of the combustion synchronised with the attainment of maximum pressure, and attributed the marked disparity between the observed pressures (bomb C) and those calculated from the heats of combustion (on the assumption of adiabatic conditions) to a rapid increase in the specific heats of steam and carbon dioxide at high temperatures. They considered it improbable that dissociation phenomena play any conspicuous part in limiting the pressures attained.

Mallard and Le Chatelier (*l.c.*) who used a Bourdon gauge for measuring pressures and applied a 'cooling correction' to their results, arrived at practically the same conclusion as Berthelot and Vieille (Ann. Chim. Phys. [vi.] 4, 13) respecting both the increase of the specific heats of steam and carbon dioxide with temperature and the small if not negligible influence of dissociation. They calculated that the temperature of the flame when moist electrolytic gas is exploded in a closed vessel at atmospheric pressure is about 3350°, and that the mean molecular heat of steam at constant volume

[1] Annales des Mines, sec. viii. vol. 4.
[2] Ann. Chim. Phys. (vi.) 4, 13.

between 0° and 3350° is 16·6. In the case of the mixture $2CO + O_2$ they concluded that the molecular heat (C_g) of carbon dioxide rises to 13·6 at 2000°, above which temperature dissociation comes into play.

Dugald Clerk also made experiments with hydrogen-air mixtures in a large cast-iron vessel comparable in dimensions to the cylinder of a six-horse-power gas engine. It was a cast-iron cylinder truly bored out and the end covers turned, internal dimensions 7 inches diameter and 8¼ inches long, capacity 317 cubic inches. Upon the upper cover was placed a Richards indicator, in which the reciprocating drum had been replaced by a revolving one; the rate of revolution was adjusted by a small fan, a weight and gear giving the power. The cylinder was filled with the explosive mixture to be tested, the drum set in motion, the pencil of the indicator pressed gently against it, and the electric spark passed within the cylinder. The pressure of the explosion, acting upon the indicator piston, traced a line upon the drum which showed the rise and fall of pressure. The rising line traced the progress of the explosion, the falling line the progress of loss of pressure by cooling.
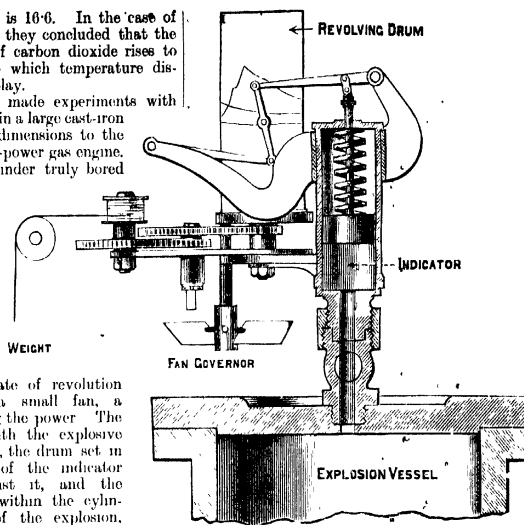

Fig. 9.

Fig. 9 shows the arrangement of the apparatus. Experiments with hydrogen and air mixtures gave the following results :—

MIXTURES OF HYDROGEN AND AIR (CLERK).

| Experiment | Mixture | | Max. pressure above atmosphere in lbs. per sq. inch. | Time of explosion | Max. temp. of explosion |
	H	Air			
			Temp. before explosion 16°. Pressure 14·7 lbs.(atmospheric)		
a	1 vol.	6 vols.	41	0·15 sec.	826° to 909°
b	1 vol.	4 vols.	68	0·026 sec.	1358° to 1539°
c	2 vols.	5 vols.	80	0·01 sec.	1615° to 1929°

The maximum temperatures were calculated on the two extreme assumptions of complete contraction and no contraction.

The curves of explosion from which these figures are deduced are given at Fig. 10.

The rate of cooling was comparatively slow; for instance, in all these experiments, at the end of 0·66 second from the beginning of explosion there still remains above 20 lbs. per sq. inch above atmospheric pressure. The explosion was followed by a very slow fall of pressure.

Calculating from these curves the total heat accounted for by maximum pressure, and allowing for loss of heat to the walls during time of
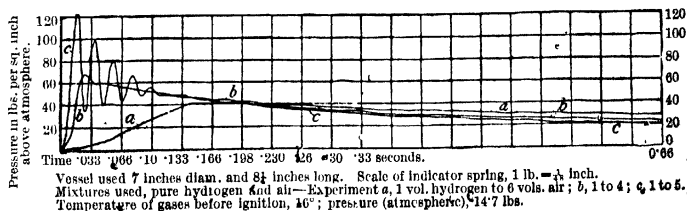

Vessel used 7 inches diam. and 8¼ inches long. Scale of indicator spring, 1 lb. = ¹⁄₁₄ inch.
Mixtures used, pure hydrogen and air—Experiment a, 1 vol. hydrogen to 6 vols. air ; b, 1 to 4 ; c, 1 to 5.
Temperature of gases before ignition, 16° ; pressure (atmospheric), 14·7 lbs.

FIG. 10.

explosion, as estimated from the falling curves, a great deficiency becomes evident.

Experiment	a	b	c
Heat of combustion of hydrogen present	100	100	100
Heat accounted for by maximum temperature and loss previous to its attainment.	55	70	54

Even with hydrogen and air mixtures the deficiency ranges from 30 to 46 p.c. It is remarkable that the deficiency at the temperature of about 900° is ·identical with that at about 1800° within the limits of error. It should be noted, however, that this method of allowing

for heat loss will probably give a low value, as no account is taken of the difference in the action of the walls on the rising and falling lines, nor of the possible difference in radiation.

In 1915 W. A. Bone and his collaborators published the results of experiments in which mixtures corresponding to (1) $2H_2+O_2+4N_2$; (2) $2CO+O_2+4N_2$, and (3) $CH_4+O_2+4N_2$, were exploded at an initial pressure of 50 atmospheres in a spherical bomb (capacity=275 c.c.) to which was attached a Petavel recording manometer with its optical accessories. The results of two typical experiments with each of the three mixtures are recorded in the following table :—

W. A. BONE'S PRESSURE EXPERIMENTS.

Mixture fired .	$2H_2+O_2+4N_2$		$CH_4+O_2+4N_2$		$2CO+O_2+4N_2$	
Per cent. composition of mixture fired	$H_2=29\ 6$ $O_2=14\cdot5$ $N_2=55\cdot9$	$H_2 \cdot 29\ 7$ $O_2=14\ 3$ $N_2=56\cdot9$	$CH_4=16\ 7$ $O_2=17\cdot1$ $N_2=66\ 2$	$CH_4=16\cdot8$ $O_2=16\cdot8$ $N_2=66\cdot4$	$CO=28\cdot1$ $O_2=14\cdot0$ $N_2 \cdot 57\ 9$	$CO=28\cdot03$ $O_2=14\ 60$ $N_2=57\cdot37$
Initial pressure p_i in atmospheres	53·0	50 0	44·9	50 0	51 0	49·8
Maximum explosion pressure in atmospheres p_m	425 0	400·0	240 0	280·0	423·0	420·0
Final pressure of cold products in atmospheres p_f	30 5	28 74	47·1	51·7	42·6	41·46
Ratio p_m/p_i	8·0	8·0	5·35	5·6	8·3	8·4
Ratio p_f/p_i	0·575	0·575	1·049	1·034	0·832	0·837
Time required for attainment of maximum pressure in seconds	0 011	0 010	0·05	0·08 about	0·10	0·10

The pressure records which are reproduced in the following diagrams (Figs. 11, 12, and 13), in which pressures in atmospheres are plotted against time in seconds, prove conclusively the absence of any direct relation between the actual rate at which the potential energy of an

explosive mixture is transferred on explosion as sensible heat to its products and the magnitude of the chemical affinity between its combining constituents. This is hardly to be wondered at, seeing the extreme rapidity of chemical interaction at high temperature as compared with
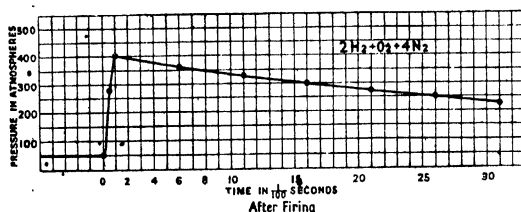

FIG. 11.

the rate at which the liberated heat can be communicated to and uniformly distributed amongst the products by ordinary physical processes. Attention may be drawn to the extreme slowness of the cooling in each case after the attainment of maximum pressure; this has also been observed by previous workers in other similar cases of gaseous explosions. This was particularly marked in the case of the methane-air mixture, in which there was hardly any appreciable cooling during an interval of

0·22 seconds after the attainment of maximum pressure (in 0 08 sec), a circumstance which may be due in part to the combustion taking place in well-defined chemical stages, and in part also to the operation of the exothermic secondary interaction between carbon monoxide and steam during the cooling period. On the other hand, the curve for the hydrogen-air mixture, where the combustion to steam is a direct and comparatively simple transaction suggests that the attainment of maximum

pressure is succeeded by a period of gradual cooling uninfluenced by chemical combination.

It may be taken as the common experience of all investigators since Bunsen's day that the maximum effective pressures recorded when gaseous mixtures are fired in closed vessels are always considerably less than those calculated on the old assumption (now discarded) that the whole heat of combustion is communicated without loss to the products, and that the specific heats of the products do not vary with temperature. Another feature of the phenomenon is the very short time required for the attainment of maximum pressure relative to the subsequent cooling period.
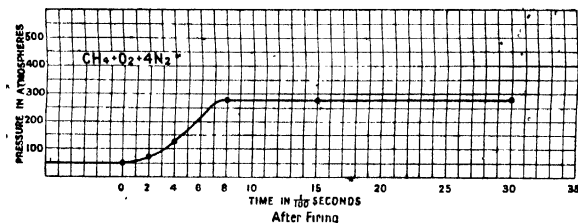
The great disparity between the found and

Fig. 12.

'calculated' maximum pressures has been attributed by the various investigators, concerned to one or other of the following causes, namely :

1. *To the marked increase in the specific heats of steam and carbon dioxide with temperature.*

2. *To the fact that in ordinary gaseous explosions, where detonation has not been determined,* combustion is by no means instantaneous, and may not be completed within the period required for the attainment of maximum pressure. Sir Dugald Clerk put forward this suggestion as long ago as 1886 [1] in criticising the conclusions of Mallard and Le Chatelier respecting the great increase in the specific heats of steam and of carbon dioxide with temperature. He considered it highly
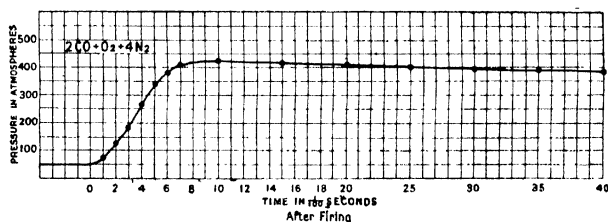

Fig 13.

probable that combustion extends far into the actual 'cooling period' in gaseous explosions (and hence the long drawn-out 'cooling curve'), so that the system loses a certain part of the heat of combustion before the chemical action is completed. This idea of a continued combustion finds support in H. B. Dixon's photographic researches, and chemists generally will concede its reality in any gaseous combination in which detonation is not determined. But to what extent it may be held to affect the pressures actually recorded by explosions is still a matter of conjecture.

3. *To loss of energy by direct radiation.*— Thus in the explosion of a mixture of hydrogen and oxygen it is conceivable that the *initial* action results in the formation of an intensely vibrating molecular complex from which steam, issues as the first recognisable product. Some experiments made in 1890 by Robert von Helmholtz (Beiblätter, 14, 589), showed that non-luminous hydrocarbon flames radiate about

5 p.c. of the heat of combustion of the gas, and more recent experiments by Callendar and Nelson show that the heat radiated from an ordinary non-luminous Bunsen flame may amount to between 15 and 20 p.c. of the total heat of combustion.

4. *To dissociation of products* (steam and carbon dioxide). In the case of two combining gases producing a dissociable product, it is clear that if the average temperature in the system reaches that at which dissociation begins the combustion must be delayed whilst heat escapes from the system by radiation and conduction. Qualitatively the partial dissociation of steam and carbon dioxide has been proved at temperatures which are certainly exceeded by those of explosion flames; but it may be urged that, inasmuch as all experiments upon dissociation have up to the present involved contact with hot solid surfaces, there is no positive evidence that the phenomenon would

[1] Proc. Inst. Civil Engineers, 85.

play any conspicuous part in an unconfined gaseous system. On the other hand, there is direct experimental evidence of the attainment of enormously high temperatures in the explosion wave, temperatures which would generally be considered as far beyond that of the initial, or perhaps even of the complete, dissociation of steam or of carbon dioxide. Moreover, the fact that the rate of explosion of electrolytic gas is retarded rather more by an excess of oxygen than by a corresponding excess of nitrogen is inconsistent with the supposition of any appreciable dissociation of steam in the explosion wave, and photographic records give no evidence of continued combination in the rear of the wave except where there are two or more chemical stages in the combustion.

Explosion of mixtures of coal gas and air.— Experiments were made many years ago by Clerk with mixtures of coal gas and air in the explosion apparatus already described, with the following results :—

GLASGOW COAL GAS AND AIR MIXTURES (CLERK).

		Temperature of gases before ignition, 18°. Pressure of atmosphere (14·7 lbs.)		
Experiment	Proportion of gas by volume	Maximum pressure in lbs. per sq. inch above atmosphere	Maximum temperature centigrade	Time of explosion
a	1/1·1	52	1047°	0·28 second
b	1/1·2	63	1265°	0·18 ,,
c	1/1·0	69	1384°	0·13 ,,
d	1/8	89	1780°	0·07 ,,
e	1/6	96	1918°	0·05 ,,

From these experiments, it will be observed that the greatest possible pressure exerted by a mixture of Glasgow coal gas and air at atmospheric pressure and temperature was 96 lbs. per square inch above atmosphere, the maximum pressure falling as dilution with air increased, while the time of explosion also increased. The shortest time of explosion was $\frac{1}{20}$ second, and the longest over $\frac{1}{2}$ second, at the end of 0·60 second from 30 to 35 lbs. per square inch pressure above atmosphere still remained in the vessel. It is very noticeable that, volume for volume, coal gas produced higher pressure than hydrogen.

Experiments with Oldham gas and air gave the following results :—

OLDHAM COAL GAS AND AIR MIXTURES (CLERK).

		Temperature of gases before ignition, 17°. Pressure of atmosphere (14·7 lbs.)		
Experiment	Proportion of gas by volume	Maximum pressure in lbs. per sq. inch above atmosphere	Maximum temperature centigrade	Time of explosion
a	1/15	40·0	806°	0·45 second
b	1/14	51·5	1033°	0·31 ,,
c	1/13	60·0	1202°	0·24 ,,
d	1/12	61·0	1220°	0·17 ,,
e	1/10	78·0	1557°	0·08 ,,
f	1/8	87·0	1733°	0·06 ,,
g	1/7	90·0	1792°	0·04 ,,
h	1/6	91·0	1812°	0·055 ,,
i	1/3	80 0	1595°	0·16 ,,

The greatest pressure produced by a mixture of this gas and air was 91 lbs. per square inch above atmosphere. Comparing these numbers with the Glasgow gas experiments, it appears that with $\frac{1}{10}$ vol. of Oldham gas present, the pressure attained was 0·5 lb. per square inch less, and the time of explosion is 0·31 second against 0·28 second with the same proportion of Glasgow gas. With $\frac{1}{8}$ of the two gases, Oldham was 5 lbs. less maximum pressure and 0·055 second against 0·05 second Glasgow.

In all these experiments the suppression of heat at the maximum temperature is very considerable, ranging from 50 to 60 p.c.

Experiments were also made by Clerk in the same vessel with mixtures previously compressed, and it is found that the pressures produced with any given mixture are proportional to the pressure before ignition—that is, with a mixture of constant composition double the pressure before explosion, keeping the temperature constant, doubles the pressure of explosion.

In 1900 Clerk made further experiments with London coal gas and air, with very complete precautions to ensure mixing, and with more accurate timing devices. The curves obtained with this apparatus are shown at Fig. 14, and the maximum temperatures and pressures, and time of explosion for the different mixtures, are as follows :—

EXPLOSION IN A CLOSED VESSEL (CLERK, 1900).
Mixtures of air with London coal gas.
Temperature before explosion 16°
Pressure before explosion . 14·8 lbs. per sq. in.

Mixture		Max. pressure above atmosphere in lbs per sq. inch	Temp. of explosion from observed pressure	Time of explosion
Gas	Air		°C.	sec.
1 vol.	12 vols.	4	—	—
1 ,,	11 ,,	58	1150	0·290
1 ,,	10 ,,	60	1155	0·305
1 ,,	9 ,,	65	1270	0·155
1 ,,	8 ,,	77	1475	0·087
1 ,,	7 ,,	80	1565	0 067
1 ,,	6 ,,	85	1660	0·055
1 ,,	5 ,,	87	1710	0·042
1 ,,	4 ,,	93	1830	0·045

J. E. Petavel has also made experiments on the explosion of coal gas and air compressed before ignition to pressures of over 1000 lbs. per square inch. Fig. 15 shows the diagrams obtained, with the particulars marked thereunder.

In all these experiments, it is clear that if the temperature be calculated from the maximum pressure of explosion, there is apparently a suppression of heat at a very considerable amount at maximum temperature, the amount being about 60 p.c.

Important experiments were also made by Prof. B. Hopkinson, of Cambridge University, who investigated the actual temperatures reached during explosions of coal gas and air in an explosion vessel of the form shown at Fig. 16 and found very large temperature variations at different parts of the vessel, and that the temperature differences existed after complete inflammation, quite independently of the local cooling effect of the walls of the vessel.
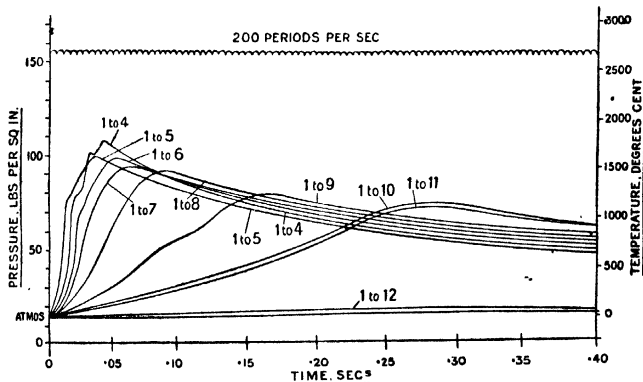

Explosion in a closed vessel, London gas, 1900 (Clerk).

He found that after the explosion of coal gas and air in the vessel, the distribution of temperature at the moment of maximum pressure was roughly as follows :—

Mean temperature (inferred from pressure) 1600°
Temperature at centre of vessel, thermometer B . . . . 1900°
Temperature 10 cm. (4 inch) within wall, thermometer C . . . 1700°
Temperature 1 cm. (0·4 inch) from wall, at end, thermometer D . 1100° to 1300°
Temperature 1 cm. (0·4 inch) within wall at side . . . . 850°

Half a second after maximum pressure, the distribution was as follows :—

Mean temperature (inferred from pressure) . . . . 1100°
Mean temperature, exclusive of layer 1 cm. thick at walls, determined by long platinum wire from B to D . 1160°
Temperature at centre of vessel, thermometer B . . . 1100° to 1200°

Here the temperature differences are much smaller than at the moment of maximum pressure. Hopkinson found that the explosion vessel is entirely filled with flame when the pressure reaches 70 lbs., although the maximum pressure attained later is 82 lbs. per square inch above atmosphere ; that is, maximum pressure is not attained until one-thirtieth of a second after the vessel is completely filled by flame. Hopkinson's experiments also distinctly prove that the highest temperature reached in the vessel is at the point of origin of the ignition, and is due to the compression of the gases which are first heated by explosion to about 1200°, and then compressed by the compression from the walls inwards, as the mixture near the walls inflames.

Explosion in gas-engine cylinders.—In all internal-combustion engines in general use at the present time, the mixture of fuel and air is compressed before ignition, the maximum temperature ranging from 1200° to 2500° ; while the temperature of the hot gases at the moment of opening the exhaust valve may be

about 1000°. Fig. 17 is a repro-
duction of an indicator diagram of
an internal-combustion engine work-
ing on the Otto cycle. The effect of
weakening the mixture is shown by
the different lines on the diagram.
The line *q* shows a diagram obtained
from a strong mixture; *b*, a diagram
from a slightly weaker mixture; and
c, a diagram obtained from a very
weak mixture. The effect of apparent
suppression of heat appears on the
gas-engine diagram as well as in the
diagrams obtained by explosion in
closed vessels at constant volume,
referred to above; and it is ex-
tremely important, for the purpose
of a correct theory of the internal-
combustion engine, to ascertain
exactly what takes place on ex-
plosion, and immediately after ex-
plosion of the mixture used; and a
complete knowledge of the thermal
properties of the working fluid and
its chemical composition at any instant during
the cycle is necessary.

In the normal gas-engine diagram, the
expansion line is at first usually considerably
above the adiabatic, showing that the whole of
the heat of combustion is not added before
maximum pressure, and that heat must be added
to the gases during a portion of the expansion,
to make up for the flow of heat through the
cylinder walls. If, however, the cooling on
expansion is too great, the expansion line may
fall below the adiabatic, although there is still
heat being added. The adiabatic expansion line
for any given mixture of gases depends on the
specific heat of the mixture, and therefore, in
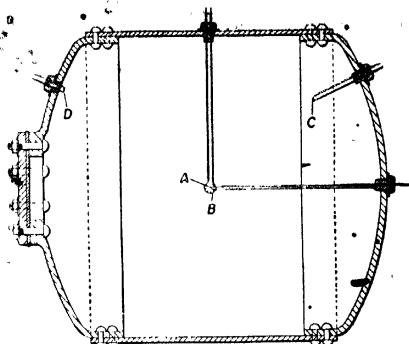order to determine what are the conditions as

FIG. 16.

Hopkinson's Explosion Vessel.

regards addition of heat, it is necessary to know
the specific heat or internal energy of the mixture
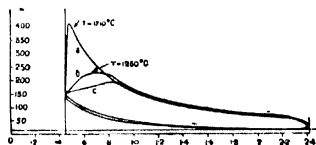at any given temperature.

FIG. 17.

Clerk has investigated the properties of the
working fluid in the gas
engine itself, by a method
which allowed direct ob-
servation to be made upon
an actual charge taken
into the engine in the
ordinary operations of its
cycle. The method con-
sisted in subjecting the
whole of the heated pro-
ducts of combustion to
alternate compression and
expansion, within the
engine cylinder, while the
cooling proceeded, and
observing by the indicator
the successive pressure
falls from revolution to
revolution, together with
the temperature and pres-
sure rise and fall due to
the alternate compression
and expansion. The engine
was set to run at a given
speed, and after the
charge of gas and air had
been drawn in, compressed
and ignited, the exhaust
valve and inlet valve
were prevented from
opening, so that when
the piston reached the
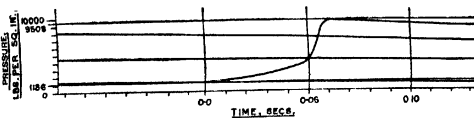
Spherical enclosure capacity, 551·9 c.c   Temperature of enclosure : before firing,
18°C.; after firing, 24°C.   Initial pressure, 1136 lbs. per sq. inch.

Maximum pressure, 9508 lbs. per sq. inch.   Ratio $\frac{Air}{Gas} = 6\cdot0$.

Ratio $\frac{Maximum\ pressure}{Initial\ pressure} = 8\cdot36$.
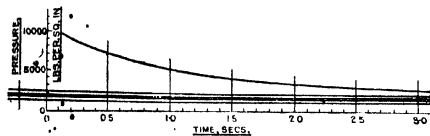
Spherical enclosure capacity, 551·9 c.c.   Temperature of enclosure : before
firing, 21°C.   after firing, 27°C.   Initial pressure, 1094 lbs. per sq.
inch.   Maximum pressure, 9618 lbs. per sq. inch.   Ratio $\frac{Air}{Gas} = 5\cdot71$.

Ratio $\frac{Maximum\ pressure}{Initial\ pressure} = 8\cdot8$.

FIG. 15.

Rise and Fall of Pressure during and after Explosion (Petavel).

end of its power stroke, the exhaust gases were retained within the cylinder, and compressed by the piston to the maximum volume, and again allowed to expand and again compressed, and so on. These operations gave a diagram as shown at Fig. 18. From this diagram, by determining the temperature fall due to work done on expansion, Clerk determined the apparent specific heat of the products of combustion, and found that for the gas-engine mixture there was a considerable rise of apparent specific heat with temperature, and it seemed probable that this was largely due to a real increase of the actual specific heat or internal energy of the gases at high temperatures. The experiments, however, could not differentiate between the possible effects produced by dissociation and real specific heat change. Further, the values obtained were subject to some uncertainty, due to the difficulty of apportioning heat loss between successive compression and expansion lines, and it is probable that the values are somewhat raised by some film phenomena, or by smouldering combustion, tending to keep the expansion line from falling as rapidly as it would otherwise do.

Work of the British Association Committee on Gaseous Explosions.—Owing to the great importance to the theory of the internal-combus-

tion engine of a complete understanding of the phenomena of gaseous explosions, the British Association appointed a committee for the purpose of investigating the whole matter, and although the work of this committee is not yet completed, very important results have already been obtained. These are set out in the Reports of 1908, Dublin; 1909, Winnipeg; and 1910, Sheffield. The committee regard it as proved that on the explosion of gaseous mixtures with air, the quantity of carbonic acid or steam dissociated at the temperature of the explosion is so small, that the suppression of heat cannot be due to this cause.

They also concluded that chemical equilibrium is complete within an extremely short period after inflammation at any point outside the influence of the walls, and that there is no time rate of combustion, such as will account for the apparent suppression of heat.

The committee have also made a very careful comparison of the specific heat found by Holborn and Henning by methods not depending on explosion, with the values found by explosion experiments, such as those of Clerk, Mallard, and Le Chatelier, and Langen. The results given in calories per gram-molecule for the internal energy calculated from 100° at temperatures of 800°, 1200°, 1600°, and 2000°, are as follows :—

| | 800° | | 1200° | | 1600° | 2000° |
	Clerk	Holborn and Henning	Clerk	Holborn and Henning	Langen	Langen
Air .	—	3570	—	5840	8760	11500
CO_2 .	—	6460	—	10880	17000	23300
H_2O .	—	4670	—	7930	14400	19900
Gas-engine mixture .	4250	3840	6900	6340	9800	13200
Ideal gas* .		3430		5400	7350	9300

* $C_v = 4.9$.

In this table, in order to reduce to foot-lbs., the figures should be multiplied by the factor 3.96.
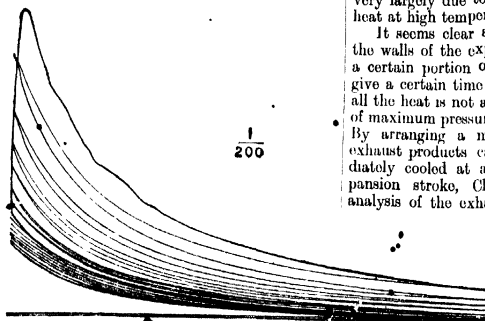

FIG. 18.

Clerk diagram from engine at a brake load of 50 H.P. at 160 revolutions per minute.

The agreement between the figures by the two methods shows that the suppression of heat is very largely due to increase in the real specific heat at high temperatures.

It seems clear also that the cooling due to the walls of the explosion vessel will damp out a certain portion of the combustion, and thus give a certain time rate of combustion, so that all the heat is not actually evolved at the point of maximum pressure or maximum temperature. By arranging a moving piston so that the exhaust products can be collected, and immediately cooled at any instant during the expansion stroke, Clerk has shown from an analysis of the exhaust products that there is still some uncombined gas after the point of maximum temperature has been reached, even with strong mixtures.

The committee also consider that the apparent suppression of heat in explosion experiments, when temperature is calculated

from pressure, is partly due to under-estimation of the heat loss due to radiation. Callendar predicted that this would be the case from his experiments on the radiation from a Bunsen flame; and Hopkinson has shown that the total heat radiated during and after an explosion of a 15 p.c. mixture of coal gas and air amounted to over 22 p.c. of the whole heat of combustion.

W. A. B. and R. V. W.

END OF THE SECOND VOLUME